1999

Mercury and methylmercury in the sediments of Lake St. Clair (Michigan, Ontario).

Andrew David. Toms
University of Windsor

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MERCURY AND METHYLMERCURY IN THE SEDIMENTS OF LAKE ST. CLAIR

By
Andrew David Toms

A thesis submitted to the
College of Graduate Studies and Research
through the School of Physical Sciences - Earth Sciences
in partial fulfillment of the requirements
for the degree of Master of Science
at the University of Windsor

Windsor, Ontario, Canada
1999

ABSTRACT

Lake St. Clair is a wide, shallow lake situated midway between Lake Huron and Lake Erie. The lake basin has been a region of significant mercury contamination for several decades due to intense industrial activities, largely those of chlor-alkali plants located up-river. As the lake flushes very rapidly ($t_R \sim 4$ days), little sedimentation takes place, hence it was expected that most contaminants would be carried downstream to Lake Erie. The persistence of Hg in the upper sediments and biota indicates that some other processes may be at work. Inorganic mercury that has been released to the environment can be converted through bacterial and photochemical pathways to methylmercury, which is highly toxic and is an efficient bioaccumulator. It was suspected that the delta of the inflowing St. Clair River has acted as a sink while the original discharge was taking place, and now, with its large areas of marshland and standing water, it may be converting this to methylmercury and releasing it to the ecosystem. In order to investigate this, sediment core samples were collected from various sites in the lake and the delta in the summer or 1997. Previous work in quantifying methylmercury in the environment has relied largely on methods which provide indirect confirmation of methylmercury (e.g. CV-AAS, GC-ECD). As a part of this study, a method was developed to overcome this limitation. In this method, methylmercury is isolated from the sediment matrix by solvent extraction and then derivatized to form a species more amenable to separation by gas chromatography. Element – specific detection was accomplished using a microwave plasma - atomic emission detector.

ACKNOWLEDGEMENTS

First and foremost, I would like to thank my family, without whose endless moral and financial support none of this would have been possible.

I would like to express my gratitude to my advisor, Dr. Brian Fryer, for all his support through this project, and for getting my 'post-graduate' career off to such a great start.

I am grateful to everybody at the National Laboratory for Environmental Testing in Burlington who helped me out, particularly my "surrogate" supervisor, Dr. Mehran Alaee, and Don Anthony for teaching me everything I needed to know about organic extractions and gas chromatography but was afraid to ask. Also thanks to Gino, Jacques, Sean, Ivy, Wendy, Dennis, Rob, Mike, Christine, Donna, Guy, Sue, Trudy, Marg, and the rest of the 7th floor gang.

I would like to thank the two other members of my examining committee, Dr. Doug Haffner and Dr. Bill Blackburn, for their constructive comments and criticisms.

Thank-you's also go out to:

Elizabeth Chandler, Jeanie Laforge, Christine Young and Josette Reaume, for helping me grease the wheels of campus beauracracy whenever needed.

Simon Haffner for his help with the field work, bad jokes, and never second-guessing the "skipper".

Chuck Robinson of the Windsor Harbour Commission for his generosity.

Steve Smith, Steve Arneil, Bob Hess and Marie Mathe -NWRI Technical Operations, and the Officers and Crew of Canadian Coast Guard Ship *LIMNOS* for their help and hospitality.

Vi Richardson -Environment Canada (Ontario Region), for the GIS maps

Phil, Mike and Jo-Ann at the NWRI Graphic Arts Department for making me look so good at conferences.

Chuck Cox – Sport Fish Contaminant Monitoring Program, Ontario Ministry of Environment for the fish data.

Dr. Henry Longerich, Earth Sciences Department, Memorial University of Newfoundland, without whom none of this would probably have happened.

Last but not least, to Lisa, for keeping me sane through the darkest hours.

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INTRODUCTION

1.1 Quicksilver in the Modern Age:

Mercury is a well-known metallic element, which occurs as a high-density silver liquid at room temperature with very high surface tension, and is also a good conductor of electricity. Among the oldest of the known metals, it has been extracted and utilized for well over three thousand years. With a global average concentration of about 50 ng/g in surficial soils, (D'Itri and D'Itri, 1977) it is found in economically viable concentrations in relatively few mineral belts throughout the world.

Mercury is easily volatilized, and as such is widely dispersed through the natural environment. It will readily bind with other elements and compounds, which has made it very useful to societies both ancient and modern; however, these same properties can render it very intractable when trying to remove it from the environment.

The effects of mercury exposure on human health have been known for almost as long as the metal itself has been in use. The Romans used to send slaves and prisoners to work the mines in Almeda, Spain, where their life expectancy was about three years. By the late 1800's, legislation had been enacted in several countries to control worker's exposure to mercury in industry. The widely quoted phrase "mad as a hatter' stems from illness arising due to the use of mercuric nitrate in the felting process used in the 19th century.

The health effects of mercury poisoning include headaches, fatigue, anxiety, loss of appetite, and emotional changes, among others -these symptoms are often vague enough that mercury may not be suspected as the cause unless an exposure to it is determined. Fortunately, unless severely high doses are received, mercury is readily excreted from most of the human organs in which it accumulates.

Far more insidious however, is methylmercury (CH_3Hg). This compound is a by-product of a number of industrial processes (principally the plastics industry), but moreover, inorganic mercury and other forms of organic mercury which are released to the environment can be methylated through several pathways and processes, both photochemically and more importantly through the action of bacteria. Unlike inorganic mercury, methylmercury bioaccumulates in the human body, where it primarily damages the central nervous system and can lead to vision impairment, loss of coordination, followed by deteriorated speech, smell and hearing, and ultimately coma and death (D'Itri and D'Itri, 1977). Sadly, it has even been discovered that methylmercury would preferentially accumulate in fetuses vs. their mothers, who could exhibit no ill effects due to partitioning through the placental barrier (Sigel and Sigel, 1997).

1.2 Noteworthy Methylmercury Incidents:

Aside from the perils associated with the production, refining, and use of mercury directly in various industries and the hazards to individual workers who came in close contact with it, the release of various mercury compounds to the environment over the

years is one of the single largest sources of indirect threats to the health of humans and ecosystems around the world.

The most famous and perhaps most chilling incident occurred in the 1950's and 60's in Minimata, Japan, to such an extent that the name (Minimata Disease) is now synonymous with methylmercury poisoning. Animals and humans began to grow ill and many died as a result of eating contaminated fish from Minimata Bay, which was receiving discharge from a chemical plant. The plant produced raw stock for the plastics industry, principally vinyl chloride and acetaldehyde, using alkylmercury catalysts in their reactor cells to the extent that 500-1000g of the catalyst was discharged for every ton of product. A number of alkylmercury compounds were also produced as by-products of the reaction, and methylmercury was one of these (D'Itri & D'Itri, 1977). The particular danger of methylmercury was realized when it was discovered that although mercury was released to the environment in numerous forms, methylmercury was the only mercury species found in the organs of the victims. The scientific community was unaware at this time that almost *any* form of mercury released to an aquatic ecosystem could be eventually methylated and accumulated in a food chain; this grim discovery would not be made until later (Sigel and Sigel, 1997).

A massive outbreak of poisoning occurred in Iraq in 1971-72, when thousands of rural villagers consumed bread made from grain that had been treated with an alkylmercury fungicide and which was intended for planting only, and not direct consumption. Unofficial estimates stated that up to 60 000 people were affected to some degree, officially (Iraq imposed a news blackout once they realized the magnitude of the

disaster they had on their hands) 6530 people were hospitalized, and 459 died (D'Itri and D'Itri, 1977).

It was at about this time that researchers in Sweden first discovered that mercury released into the environment in various forms could be converted to methylmercury, apparently through the action of anaerobic bacteria such as *Methanobacterium* and *Clostridium cochlearium* (Hamaski et al. 1995). Results such as these, as well as the disasters mentioned above and elsewhere, slowly led to widespread banning of mercury compounds as seed dressings/fungicides, and gradually tightening regulations for mercury discharges from industrial activities.

However, the legislated reduction in emissions did not come soon enough. Here in Canada two examples in particular of mercury contamination of the environment stand out.

Perhaps the most infamous incident took place on the English-Wabigoon Rivers system, in north-eastern Ontario near Dryden. A chlor-alkali plant went into operation at a pulp and paper mill in 1962, and during its subsequent operation, the reactor cells had to be re-charged with mercury to compensate for losses in quantities of 300-5500kg per year. There was heated debate among members of the scientific community, the media, and the government at the time as to whether any of the Ojibway Indians living on reservations downstream and who depended on fish as a staple of their diet had suffered from mercury poisoning or not. Due to social and political biases at the time, potential symptoms were often attributed to excessive alcohol consumption instead (D'Itri and D'Itri, 1977).

Last but not least, there is Lake St. Clair, the focus of this present study. Lake St. Clair and its main tributary the St. Clair River, received mercury discharge from a chlor-alkali facility located ~50 km upstream in Sarnia, which, while in operation, discharged up to 90kg per day of mercury effluent. (D'Itri and D'Itri, 1977) This resulted in the permanent closure of the commercial fishery on Lake St. Clair. Although levels of mercury in the fish have declined significantly over the years since the mercury cells were shut down in 1970-71, there remains a significant amount of mercury in the sediments in some areas of the lake. There is some debate as to whether atmospheric deposition from fossil fuel consumption of nearby heavy industry might still be supplying mercury into this environment today (Pirrone et al. 1995).

1.3 Study Area – Lake St. Clair:

Lake St. Clair is a wide, shallow lake situated mid-way along the Lake Huron - Lake Erie corridor, connecting these two lakes via the St. Clair and Detroit Rivers. (Figure 1-1).

Located ~5km upstream from Detroit / Windsor, the lake is approximately 40km in diameter, with an average depth of just 3m and a surface area of 1114km^2. The lake sits on a thick layer of glacial till, clays and recent sediments some 30m above the underlying bedrock.

It is densely populated along most of its shoreline, with the exception of the north-eastern corner, which is mostly marshland. Most of the delta of the inflowing St. Clair River is aboriginal territory (Walpole Island Nation). There is little industrial activity directly along the shores, but two of the other major tributaries, the St. Clair River and the Clinton River, pass through heavily industrialized areas (the St. Clair River region is also known as "Chemical Valley"), and the third, the Thames River, flows through an intensely agriculturalized region. There are three coal-fired generating plants along the St. Clair River, and an extremely high concentration of heavy industrial activity in the Detroit area. Although Lake St. Clair is by far the smallest lake within the Great Lakes system, the St. Clair River delta is the largest delta in the entire basin.

The bulk of the inflowing water (98%) comes from Lake Huron via the St. Clair River, such that the water quality of Lake St. Clair is directly influenced by that of Lake Huron. Particularly, the sediment loading of the river is proportional to the wave energy found in Lake Huron. The sediment load delivered to the lake is largely sand, and is thus largely carried as bed load along the river bottom rather than suspended load. Because Lake St. Clair itself is so shallow and has a relatively short fetch (maximum 42km), erosion within the lake is limited especially as the shallow bottom tends to dissipate wave energy before it can reach the shoreline (Bolsenga and Herdendorf, 1993). Water entering the lake has a relatively short hydraulic residence time, of approximately 9 days, and suspended fine-grained sediments take about 2 days to settle out. As a result, it can be said that the entire suspended load of the St. Clair, Thames and Clinton Rivers will

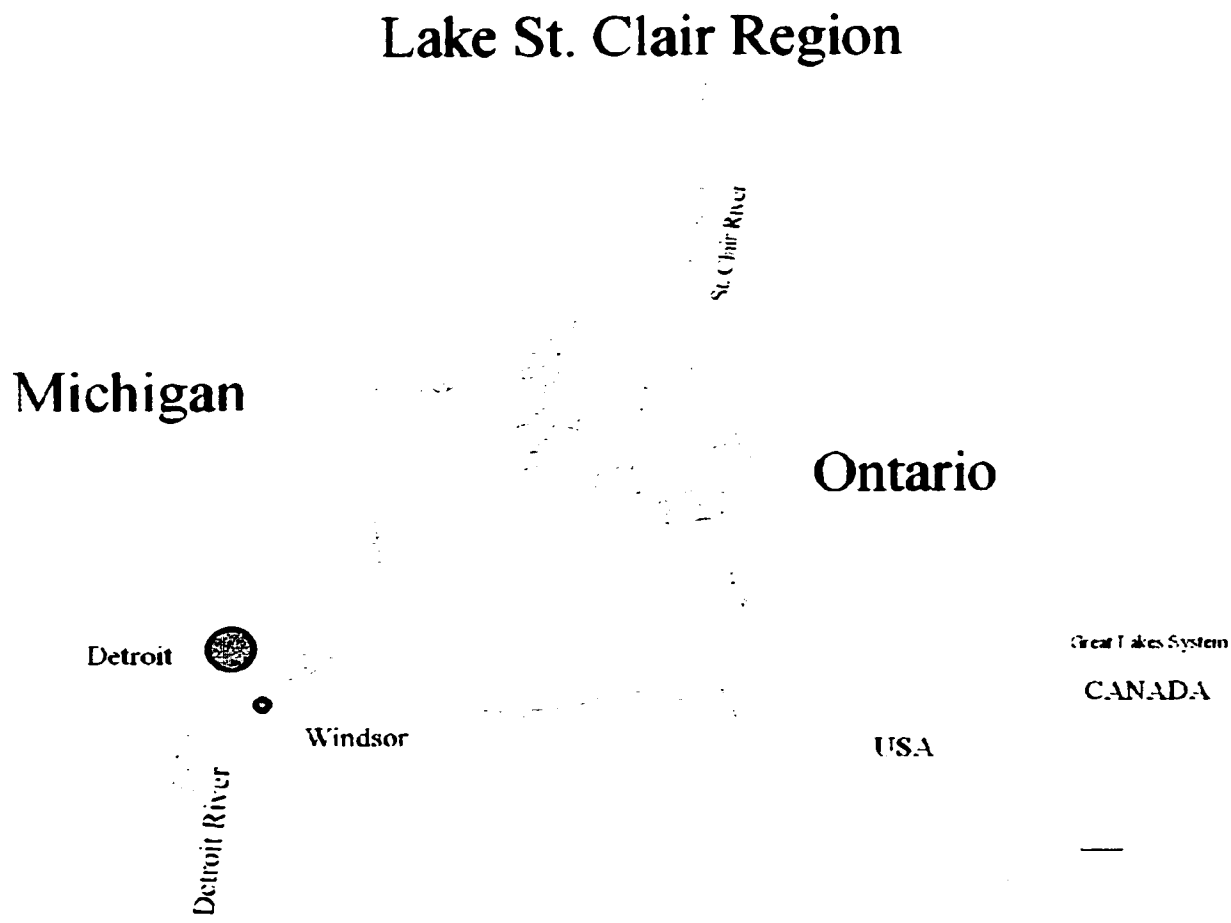

Figure 1-1. Map of Lake St. Clair and surrounding area

ultimately interact with the sediment-water interface before leaving the basin (Robbins et al. 1990). A large proportion of these suspended sediments ultimately do leave the basin, which has been classified as a non-depositional environment, based on the relative paucity of recent sediments overlying the glacial clays (Thomas, as quoted in Robbins *et al.* 1990). The recent sediments have been shown to have an average thickness of ~7cm and a maximum of ~30cm found in previous literature (Mudroch, 1989), and borne out by observations in the present study. An example of the recent sediments overlying the glacial clays can be seen in the photograph of a core sample from the lake shown in Figure 1-2. Robbins et al. (1990) studied sedimentation rates in Lake St. Clair by carrying out a radionuclide study of ^{137}Cs and ^{210}Pb in the lake basin, and determined that the lake-wide average annual accumulation of sediment was 0.06cm/yr, and determined the average age of these sediments to be 120 years. This concurs with the previous generalization of Lake St. Clair being a non-depositional environment, given the amount of time that has passed since the last Ice Age with no sediment accumulation. Moreover it can be correlated with the onset of intense settlement, deforestation, and agriculturalization of the region in the middle of the last century which could have led to much higher runoff loads being delivered to the system. As was mentioned earlier, most of the suspended sediments entering Lake St. Clair ultimately do leave the basin, and in the case of the previous radioisotope study, it was demonstrated that at the time only 8% of the ^{137}Cs was retained within the local basin. Mudroch et al. (1989) showed that the sediment in the lake had a resuspendible pool mass of ~4.5g/cm^2, which had a residence time of ~3 years.

Figure 1-2. A sediment core sample being recovered and sectioned aboard ship. The modern sediments can be seen as the darker-coloured upper third of the core, overlying the glacial clays which are of a more uniform composition.

Lake St. Clair is also noteworthy as the first site within the Great Lakes basin where zebra mussels were discovered, in 1985. Although a number of studies have been done on heavy metals accumulation by *dreissena polymorpha* (Al-Aasm et al. 1998) to date no published results on their possible interaction in mercury cycling within the Great Lakes have been found.

1.4 Objective of the Study

The Lake St. Clair ecosystem has been a region of significant mercury contamination for several decades. High levels of industrial input into the St. Clair River in the 1960's have been retained in the sediments to a substantial degree. This is contrary to predictions that mercury contamination would ultimately either be remobilized and flushed downstream to Lake Erie over time, or buried by overlying sediment accumulation.

It has been shown that during the initial period of sediment contamination, mercury loading onto the sediment was extremely high. Now that mercury levels in the inflowing river have decreased, it has been suggested that the lake bottom itself is acting as a new source of mercury into the ecosystem, since many fish species still show higher levels of contamination in Lake St. Clair to this day than in Lake Erie even though major influx was halted in the early 1970's.

This area was chosen for a study of mercury and methylmercury in sediments due to the fact that although the lake had been surveyed extensively for total mercury several times since anthropogenic contamination was first discovered, no work on the occurrence or distribution of methylmercury has been found, and no work on mercury has been published in over a decade. In light of the fact that mercury contamination of this ecosystem remains significant nearly thirty years after the major influx of mercury was halted, it was felt that a better understanding of where methylmercury might be originating from might help to understand the long-term dynamics that are taking place, particularly as organic mercury is the key exposure route for fish, and thus humans.

This project was therefore initiated to sample sediments throughout the lake basin, and to measure the amounts of total mercury and methylmercury occurring at each location. To achieve these goals, finding a suitable method for the extraction and analysis of methylmercury was also necessary.

CHAPTER TWO

EXPERIMENTAL

2.1 Site Selection

In order to obtain more detailed information about changes in the physico-chemical properties of the sediments with depth, it was decided to utilize core sampling for sediment collection rather than grab sampling, since this would enable vertical as well as spatial profiling.

Sample sites were chosen to reflect the water circulation patterns, ideally areas of calm water near major inflowing channels in and around the river delta. The desired sites were plotted on a navigational chart (NOAA #14850, 48th edition; 1:60000) and from this, co-ordinates were obtained and programmed as waypoints in a hand-held GPS receiver (Garmin GPS 45XL). No cores could be obtained at some chosen sample sites in the lake due to high sand content in the bottom substrate. The sampling locations are shown in Figure 2-1.

2.2 Coring Aboard U. of W. "Mon Ark"

Preliminary sampling of most sites was done using a Petite Ponar ™-type grab sampler (Wildlife Supply Company (Wildco) Saginaw, Michigan) to determine if the bottom substrate was suitable for coring. In many areas a hard, sandy layer that the corer could not penetrate covered the bottom. Core sampling was done using a Kajak-Brinkurst-type 2" core sampler (Wildco) which had the optional heavy (13.6kg)

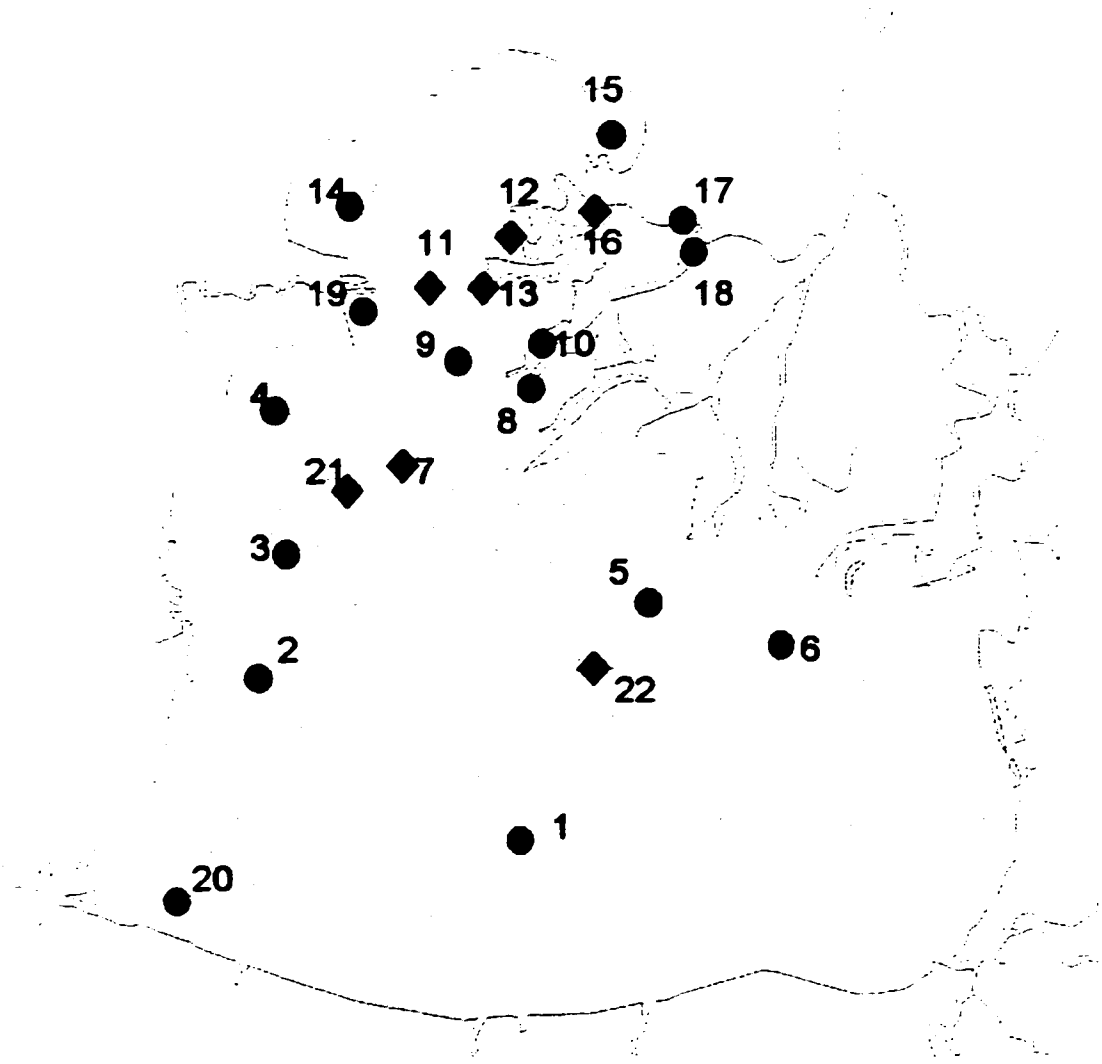

Figure 2-1. Sample locations in Lake St. Clair and St. Clair River delta.

base attached, and used replaceable Lexan ™ core liners as shown in Figure 2-2.

The sediment sampling was done from a small boat (The University of Windsor *R.V. MonArk* –See Figure 2-3) equipped with a small crane and hand winch fixed with 25m of aircraft-grade 1/16" steel cable.

The corer was dropped from the water surface by allowing the winch to free-spool, which maintained slight tension on the line and ensured the corer remained vertical as it fell. After the corer had struck bottom, the cable was drawn tight and a messenger weight was dropped to trip the spring-loaded valve closed. Once the corer had been recovered the core liner sleeve was immediately removed and sealed with watertight plastic caps, labelled, and placed upright in an ice-water bath.

Upon returning to the lab (later the same day) the cores were placed upright in a freezer at -15°C. Once the cores (still in their liners) had frozen solid overnight, they could be stored/stacked horizontally. (June – August 1997). The cores were kept frozen on ice in coolers while they were transported to National Water Research Institute in Burlington, and remained in a freezer there until they were sectioned.

2.3 Sectioning of Cores at NWRI

Slicing of the cores was done using a Teflon sheet as a working surface and a 6"x2"x1/16" Teflon section as a blade to slice the samples. A Teflon spatula was also used to extract material from the lower core sleeve cap.

Figure 2-2. Illustration of Kajak-Brinkhurst corer and Petite Ponar grab sampler used for the sediment sampling program

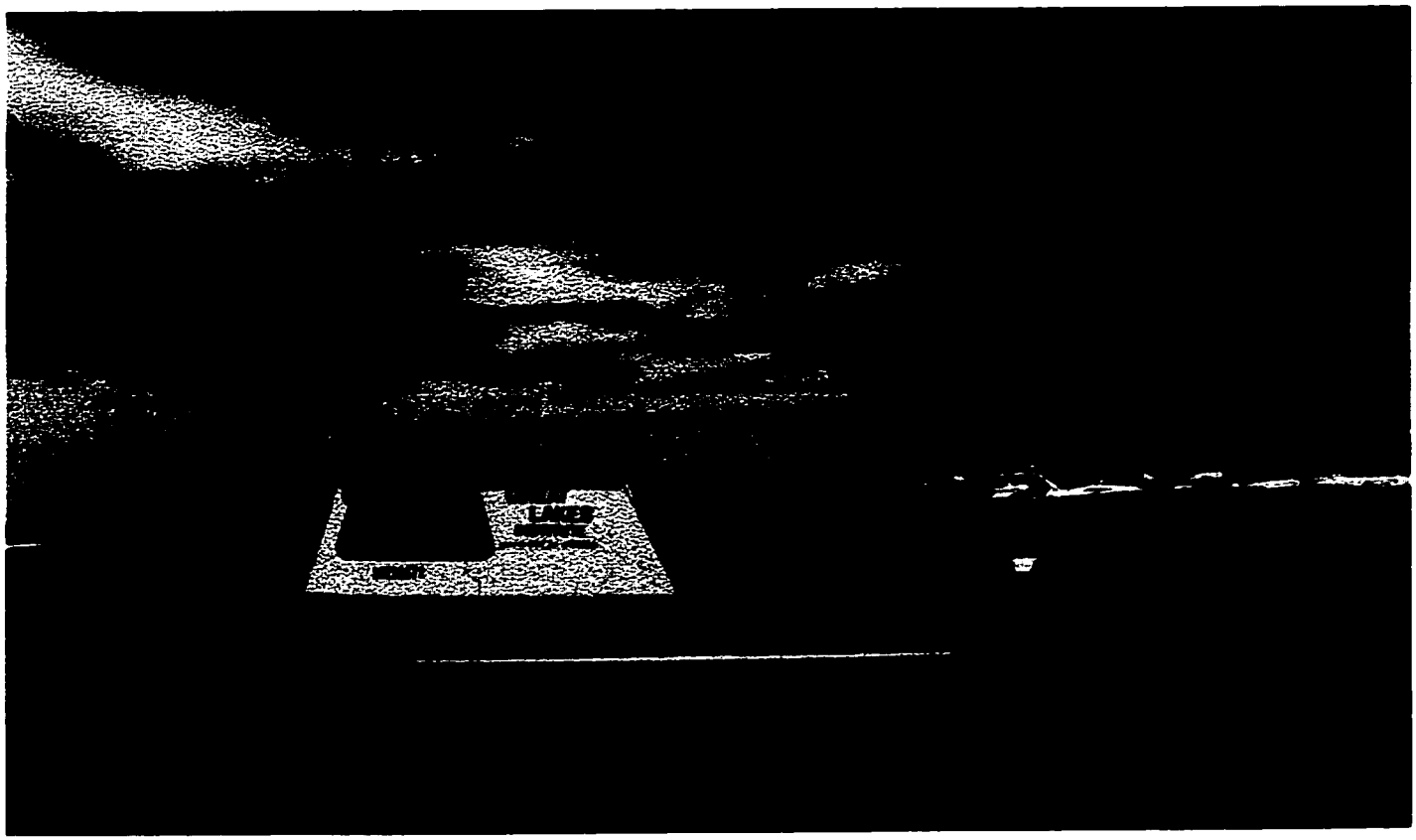

Figure 2-3. The Great Lakes Institute Research Vessel "*MonArk*"

All Teflon lab ware was washed with acetone/hexane prior to initial use, and then rinsed with deionized water between each sample.

After removing the top sleeve cap, the core was allowed to slide out while slowly raising the sleeve, in a vertical position. Once the core was almost completely out, the whole assembly was quickly laid on its side before the core could collapse under its own weight. If need be the core was pushed down from the top using a metal rod and a wad of lab tissue –the sediment coming in contact with the lab tissue was discarded.

Once the core had been extracted and was lying on the work surface, it was sliced into 5cm lengths using the Teflon blade and then each subsection was sliced in half lengthwise. These "splits" of each subsection went into two separate pre-washed 100mL screw top jars, such that one section was intended for methylmercury analysis and the other for total mercury analysis.

The jars were labeled as follows:

ATC	-	01	-	01	-	MHG
type of sample		sample#		sub-sample#		type of analysis intended

Therefore, data reported for sample 12-03, for example, would refer to site #12, at the 10-15cm depth interval. The core samples had been transferred from the freezer to the cooler approximately one week before the cores were sliced.

2.4 Coring Aboard C.C.G.S. LIMNOS

As previously mentioned, the hard, sandy bottom substrate in many parts of Lake St. Clair made coring difficult if not impossible with the equipment available at the University of Windsor. Also, it was not known if the corer was penetrating the thick glacial clays to sufficient depth to show predicted recent anthropogenic influences vs. background levels. As a result, a co-operative effort was undertaken to use a much larger and heavier coring device owned by Environment Canada, which in turn required a larger vessel to deploy it. Arrangements were made for the Great Lakes survey vessel *C.C.G.S. LIMNOS* to take several core samples in Lake St. Clair during one of its extended research cruises.

A large Benthos™ core sampler was deployed from a gantry on the ship's superstructure and raised and lowered using a variable-speed electric winch, as shown in Figure 2-4. Due to the known hard substrate on the bottom of Lake St. Clair, 80kg of auxiliary weight was attached. This corer used 6.75cm inside diameter replaceable industrial-grade PVC sleeves. Once the corer had been winched back aboard, the bottom of the core sleeve was immediately plugged with two large rubber bungs to prevent leakage. The sleeve was then removed from the corer.

The cores obtained aboard the *LIMNOS* were subdivided on-board (see below) into 1-2cm lengths (three cores were collected from the same site, and the sectioning varied among them –individual records were made of how each core was divided) and placed in 500ml pre-washed glass screw-top jars. The jars were immediately placed on ice in coolers until they were brought ashore that evening, when they were also frozen at -15°C, and then placed back in coolers to be shipped to NWRI the next day. These

samples were placed in a walk-in cooler at 4°C in Burlington. These practices for sampling and storage of mercury sediment samples were in accordance with those outlined in Horvat et al. (1993) and Gottgens et al. (1999).

Once the smaller cores (from the *MonArk*) had been sectioned at NWRI they were also stored in the cooler at 4°C until needed.

2.5 Sectioning of Cores Aboard LIMNOS

Before the cores were sectioned, the core sleeve was sawn off about 15cm above the top of the sediment-water interface (the water column above the sediment was retained in the sleeve up to this point). Once the overlying water had drained off, the core sleeve was clamped in a sealed base, and water pressure was applied to the bottom, such that the two rubber bungs acted as a piston and forced the core upwards, as can be seen in Figure 2-5. A ruler was used to measure the distance the core moved, and once it reached the upper end/lip of the core sleeve, it was sliced off with a stainless steel (cores # 1 & 2) or plastic (core #3) blade. Each slice was then placed in its own pre-washed, labeled 500mL screw-top glass jar.

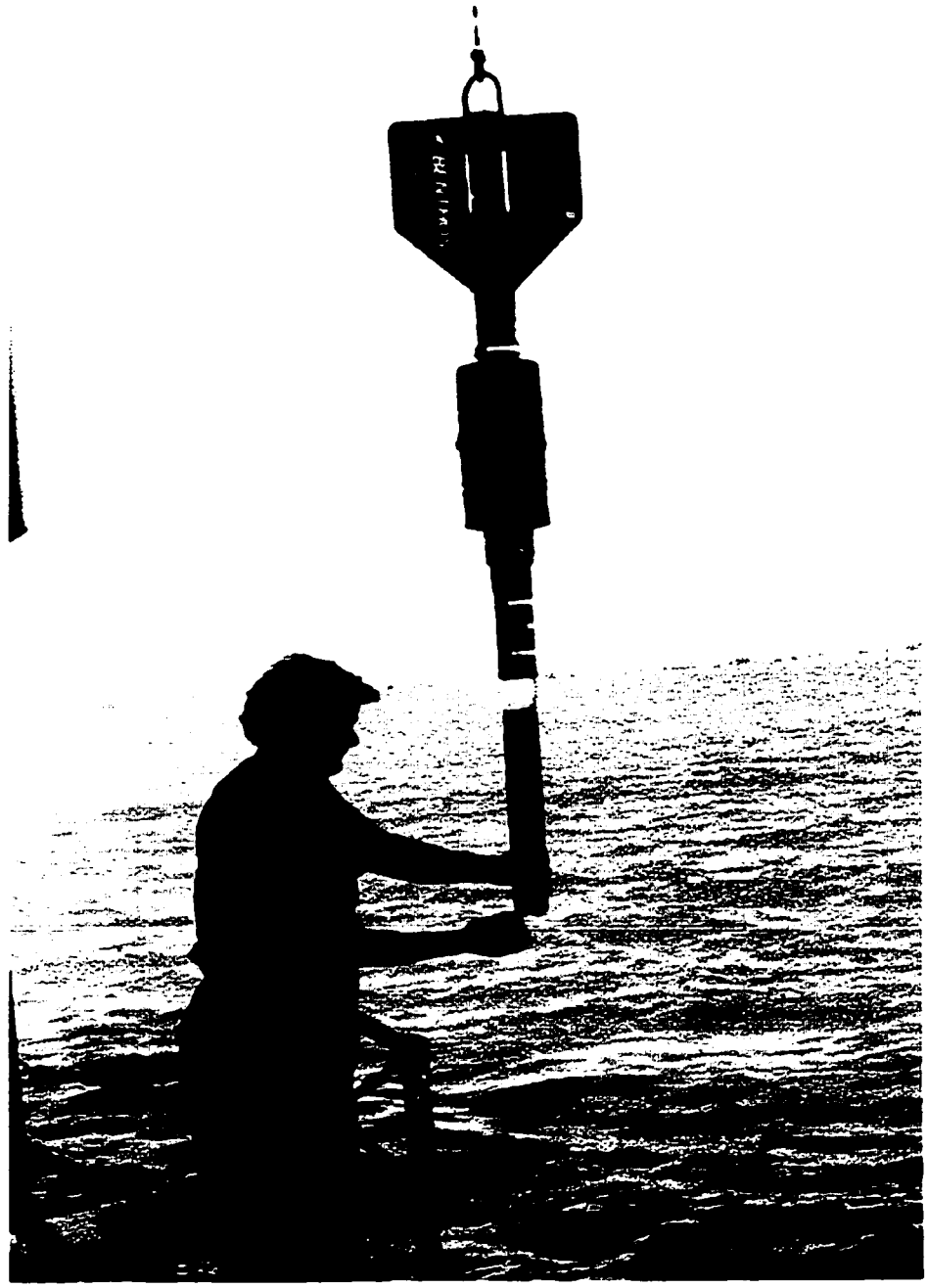

Figure 2-4. Recovering a core using the BENTHOS corer aboard the *C.C.G.S. LIMNOS*

Figure 2-5. A core being sectioned and transferred into glass jars aboard the *C.C.G.S. LIMNOS.*

2.6 Determination of Total Hg in Sediment by Flameless AA at NWRI

- The samples allotted for this analysis were retrieved from the cooler and allowed to come to room temperature. Each sample was stirred with a glass rod in its jar to obtain a more homogenous matrix.
- Following this, "plugs" of each sample were removed by forcing a glass tube into the mud, and transferring a portion into a pre-weighed 100mL volumetric flask. This technique ensured that even if the sample was too viscous to stir, a more representative cross-section could still be obtained.
- The 100mL flasks were then transferred to a fume hood and 15mL of concentrated H_2SO_4:HNO_3 in a 2:1 ratio was added in 7.5mL aliquots, allowing the reaction to subside between additions.
- 2mL of concentrated HCl was then added in 4 x 0.5mL aliquots which generated vigorous bubbling.
- The flasks were then covered (but not sealed) with plastic wrap, and left to stand.
- After sitting overnight, the flasks were transferred to a shaking water bath and agitated gently at 60°C for two hours.
- Next, 15mL of potassium permanganate solution was added in 3 x 5mL aliquots, with swirling between each addition, which were accompanied by vigourous bubbling and release of heat.

- Following the permanganate solution addition, 10mL of potassium persulphate solution was added to each flask, after which they were again covered with plastic wrap and left overnight.
- The next morning, 5mL of hydroxylamine hydrochloride was added to each flask, reducing the purple permanganate colour to a brown (coffee) colour. The flasks were then brought up to volume with ASTM Type I water (~18MΩ/cm).
- A portion of each solution was then decanted into a glass centrifuge tube (Kimax, 38mL) and centrifuged @ 2000rpm for 10 minutes.
- The tubes were then placed in an autosampler (Technicon IV) which was connected via a peristaltic pump (Carlo Erba) to a mercury atomic absorption spectrometer (Pharmacia 100-M).
- A full set of calibration standards, control standards, calibration blanks, and spikes was also prepared and analyzed for quality control purposes.

For further details see NLET Method #02-2601 (1994). This procedure was carried out according to a CAEAL-accredited protocol.

2.7 Determination of Moisture Content

At the same time that the total mercury analyses were being carried out, another portion was taken from each sample using a spatula and placed in a pre-weighed 30mL polypropylene vial, to be freeze-dried for a determination of moisture content. The remaining sediment in the jars was re-capped and returned to the cooler to be stored in

case of future need. The vials for moisture analysis were placed in a freezer at -24°C overnight. The vials were removed from the freezer the next day and placed in a vacuum chamber at 1.2torr for a minimum of 48 hours. They were then re-weighed and the % moisture content determined by difference.

CHAPTER THREE

METHYLMERCURY ANALYSIS

3.1 Introduction

Mercury analysis of a wide variety of environmental samples and matrices is a widespread practice using a number of preparative and analytical techniques. These protocols are well documented and many laboratories are accredited to national and international standards for this type of work. The most widely used method is likely the cold vapour -atomic absorption technique, by which all the mercury in a sample is digested by strong oxidants and then reduced to the mercury vapour to be determined via a flameless spectrophotometer, as described previously.

Unfortunately, such a straightforward technique as this does not exist for the determination of methylmercury. Indeed the chemistry and behaviour of methylmercury in the environment is poorly understood from the molecular to the global scale (Hintelmann et al. 1995). Because of this, neither a widely-accepted sample preparation/extraction technique, nor a routine instrumental analysis method has yet found widespread use (Caricchia et al. 1997). Furthermore, there were at the time no certified reference materials (CRMs) available for methylmercury in sediment which can be used to validate any analytical method development. This is undoubtedly related to the inherent instability and volatility of methylmercury, as well as the difficulties in extracting and measuring it accurately.

The quantitative analysis of methylmercury in environmental samples is still an evolving field. Due to the intrinsic properties of organometallic compounds, they are sometimes impossible to determine by traditional methods. Owing to its organic nature,

it is difficult to extract and isolate Methylmercury from other compounds in the same matrix. Total digestions obviously cannot be used since these would destroy the speciation present. Also, mercury compounds are not easily quantified using detection methods associated with organic analysis.

A number of published methylmercury methods do exist. They are, however, often adopted by researchers on a project-by-project basis, and many workers often end up trying to improve and modify the experiment even as they are attempting to process their own samples. Two of the most commonly used methods in the literature are CV-AAS with a back-extraction to separate the organic phase, or GC-ECD (gas chromatography - electron capture detection) (Donais et al. 1996).

Both of these methods/techniques are fairly widely available in environmental analytical laboratories, and either of these could have been carried out using facilities at the University of Windsor/Great Lakes Institute for Environmental Research. However, neither of these was utilized because each suffers from a severe drawback as well.

The CV-AAS method relies on extraction from the sediment followed by a back extraction or selective reduction to separate the organic and inorganic phases, after which the Hg content of the organic phase is determined. While this technique is highly sensitive for mercury compounds, it is not nearly as reliable for determining the speciation, as positive identification of methylmercury cannot be made in the presence of other organo-mercury species.

On the other hand, the gas chromatography-based ECD technique can easily separate and quantitate organic compounds. However, although the ECD detector is highly sensitive and widely used for environmental work, it is unable to measure mercury

directly, and so the extracted sample must be derivatized to a halide compound (such as CH_3HgCl). Therefore, although this instrumentation provides good resolution of an often complex sample matrix, it cannot directly identify mercury compounds. The problem with this is that there are a great number of different compounds in a typical environmental sample, many of which may elute during chromatographic separations at or near the same retention time as methylmercury, as was discovered during developmental work on this project (Cai at al, 1996). As an example, a chromatogram showing the large carbon response vs. mercury that is observed in a typical analytical chromatogram is shown in Figure 3-1.

Although it has been commonly assumed in the literature that mercury in biota (fish) is comprised of greater than 95% methylmercury, as reported in the review by Downs et al. (1998) recent studies have shown that this is not always the case (Wagemann et al. 1997). In fact, preliminary work on this project showed that one of the common Canadian reference standards DOLT-2 (dogfish liver tissue) for mercury in the aquatic environment potentially contained significant amounts of other organomercury compounds, as shown in Figure 3-2. Any environmental surveillance work that entailed study of piscine tissue would therefore also be well-served by a technique that could distinguish separate organomercury compounds.

A review of the two methods described above, as well as others, led to the decision to adopt a less common technique, but one that seemed to offer the advantages of both these approaches, while simultaneously overcoming their individual drawbacks: Gas Chromatography -Microwave Induced Plasma - Atomic Emission Spectroscopy

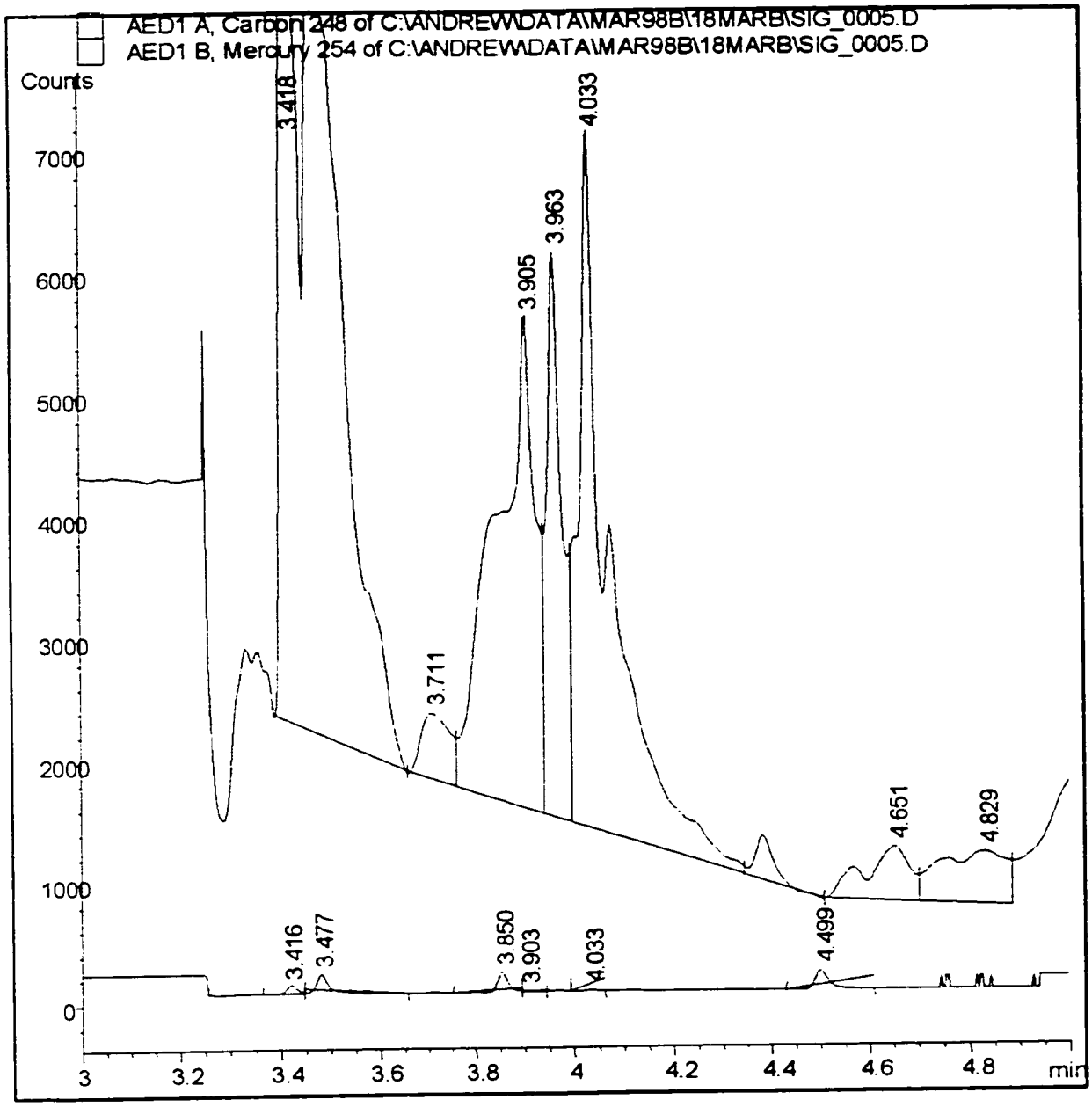

Figure 3-1. Chromatogram of carbon (upper signal) and mercury (lower signal) detector response in counts (Y-axis) vs. retention time in minutes (X-axis), overlaid on the same scale for a 50pg/uL calibration standard, illustrating the relative peak intensities of the two elements.

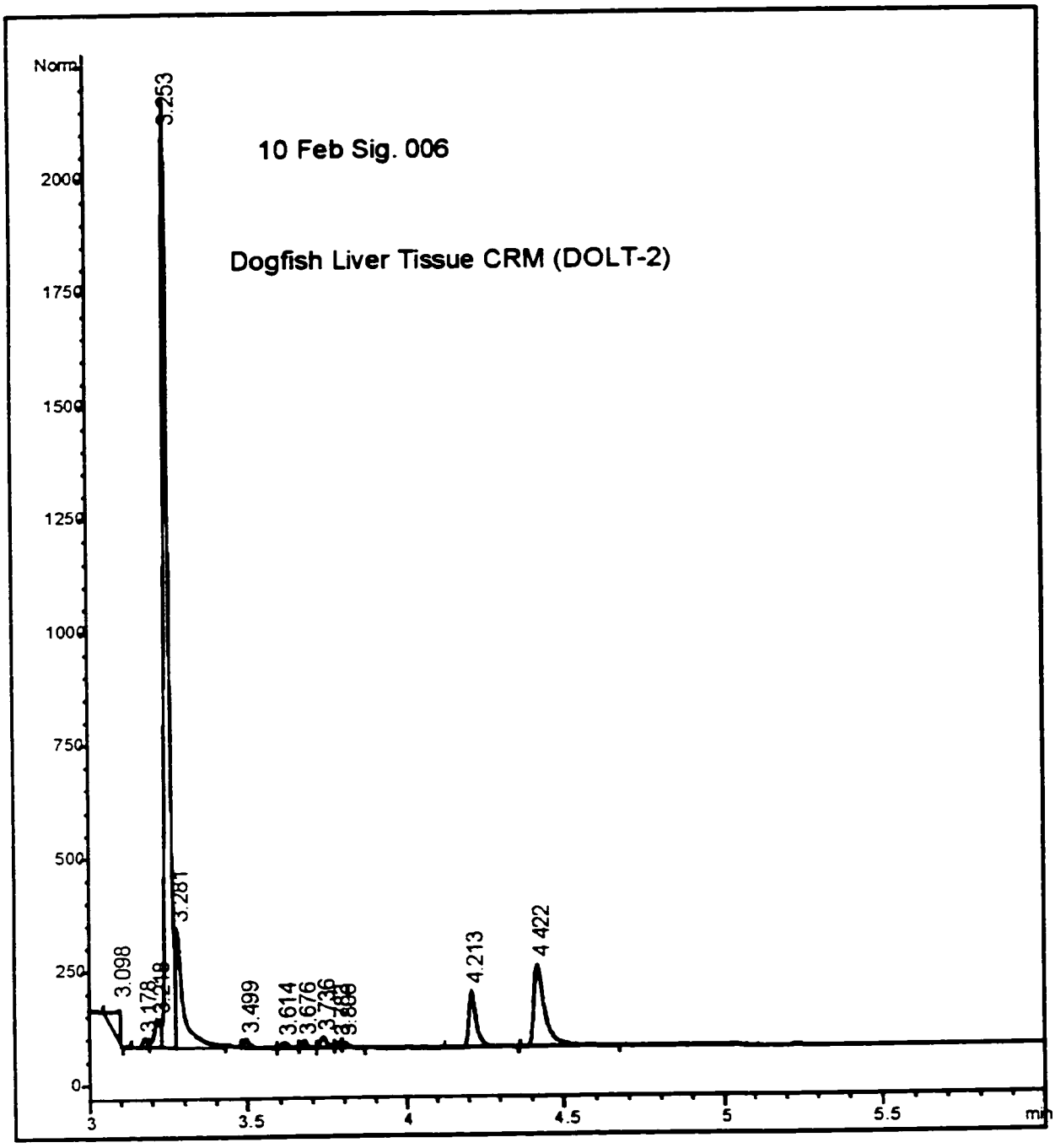

Figure 3-2. Chromatogram of dogfish liver tissue standard DOLT-2 with detector counts (Y-axis) vs. retention time in minutes (X-axis), showing an intense methylmercury signal as well as several other possible organomercury peaks.

(GC-MIPS-AES). These types of instruments have been around for about two decades, and although they are not commercially available from many manufacturers, they have also been custom-made in-house by various research groups (Emteborg et al. 1993). This instrumentation offers all the advantages of capillary gas chromatography for separation and resolution of the organic matrix, coupled with a highly sensitive and element-specific atomic emission detector described in Sullivan and Quimby (1990) shown in Figure 3-3. While gas chromatography is a very well known technique, the coupling with a MIPS spectrometer is relatively uncommon. The principle behind the microwave plasma is basically the same as in argon gas inductively coupled plasma (ICP) systems found in thousands of spectrometers worldwide with a few differences. The carrier gas is helium instead of argon, and the RF power is introduced in the microwave (GHz) energy range instead of MHz. The torch is also much smaller and totally enclosed, such that it is more compatible with the gas flow
rates associated with chromatography (~10-50mL/min) rather than the >12L/min needed to sustain typical ICP sources (Quimby et al. 1990).

While this technique is less common that those previously mentioned, other researchers have also realized its potential for environmental organometallic research, including mercury, tin, lead and arsenic compounds, and so a number of references to methylmercury analysis were found, particularly the work by Donais et al. (1996). The instrumentation used in this project was manufactured by Hewlett-Packard (Palo Alto, California) and consisted of a 5890 Gas Chromatograph interfaced with a 5921A Atomic Emission Detector (which consisted of both the microwave plasma system and the spectrometer), and will be referred to hereafter as a GC-AED, as shown in Figure 3-4.

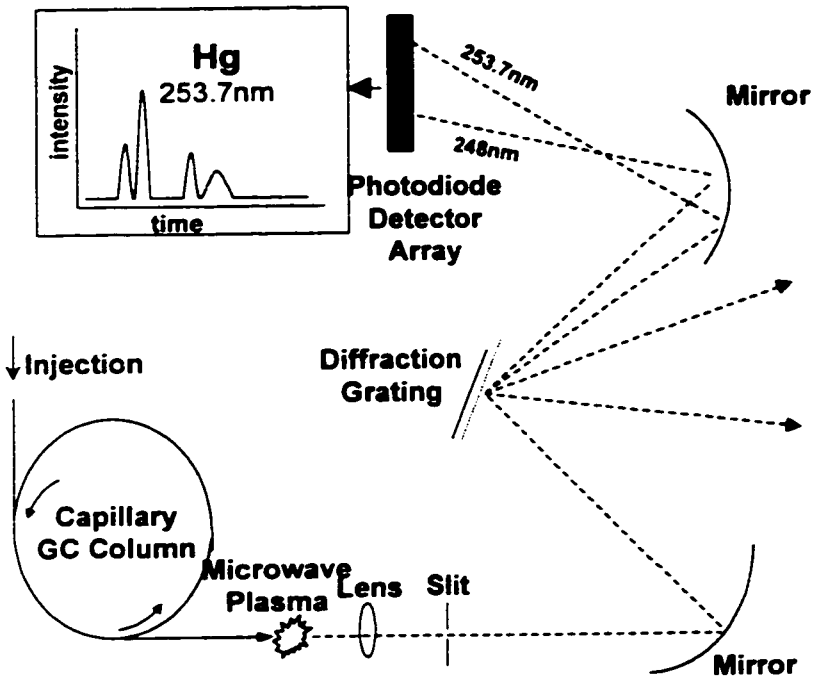

Figure 3-3. Schematic of GC-MIPS-AES system

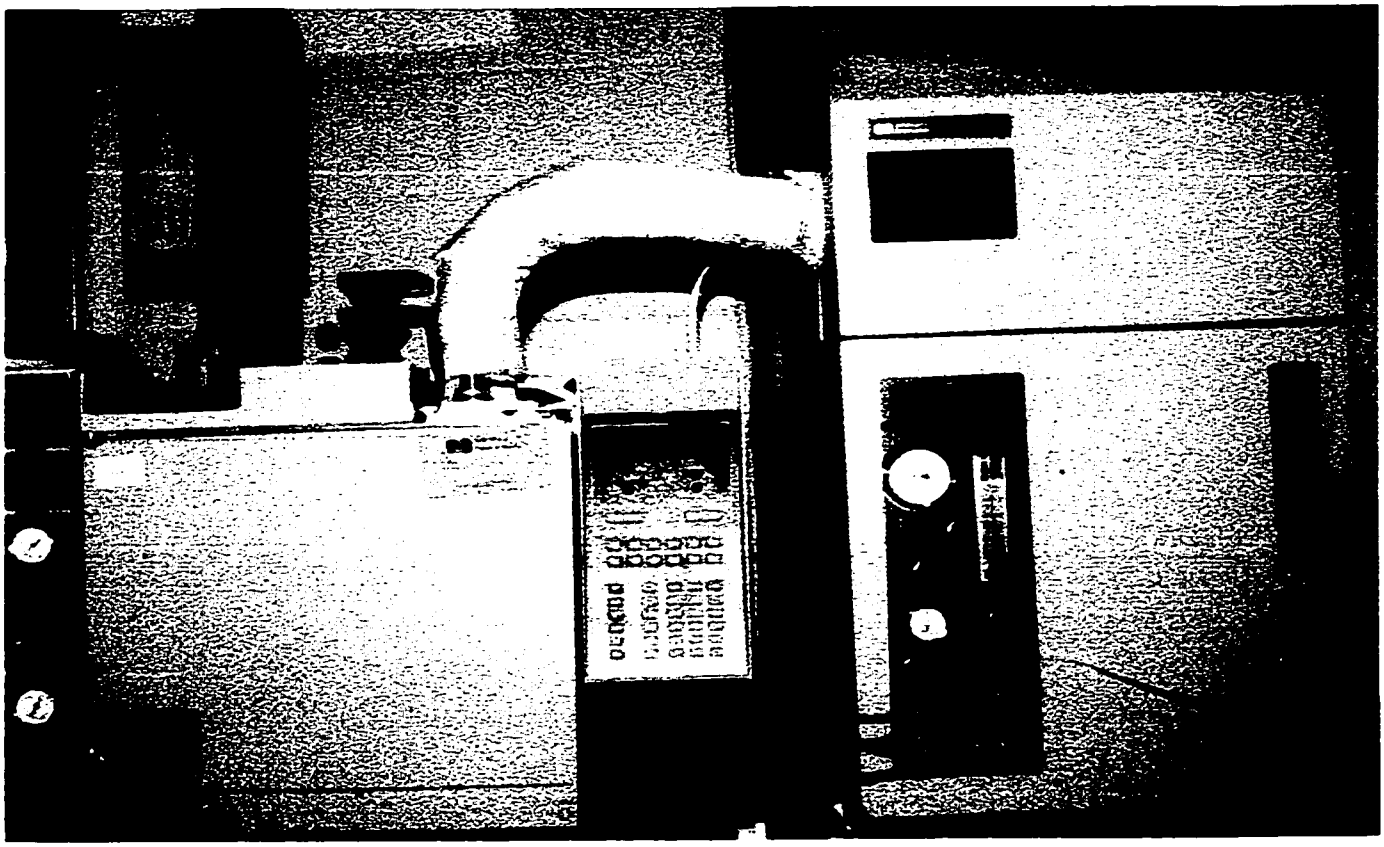

Figure 3-4. The Hewlett-Packard 5890-5921A Gas Chromatograph – Atomic Emission Detector system. The GC is on the lower left and is connected to the AED on the right via an insulated high-temperature transfer line.

Following the assessment of available literature on the subject, and the instrumentation available at the University of Windsor, a collaborative research project was developed between the Great Lakes Institute for Environmental Research and Environment Canada's National Laboratory for Environmental Testing. The NLET laboratories are a part of the National Water Research Institute and are located at the Canada Centre for Inland Waters, in Burlington, Ontario. NLET had a GC-AED system and an interest in implementing a method to analyze methylmercury in sediments and waters, but was unable to direct staff resources exclusively to the development of a methylmercury method in-house. Therefore the graduate research work was relocated to Burlington and carried out while being supported by the University of Windsor, with Environment Canada supplying the research space, equipment and technical support. This was advantageous to both parties in that a method was developed that would allow methylmercury determinations of the Lake St. Clair samples, and NLET benefited through the development of a technique that they could further refine and apply to Environment Canada's nationwide analytical sampling objectives.

In this project an attempt was made to combine the best of both of the previously described approaches, by first developing an organic-based extraction technique for separating the compound from the raw sample, and then subsequently using gas chromatography coupled with microwave plasma-atomic emission detection to isolate the various compounds in the matrix positive, and provide quantitative determination of mercury in the separated compounds.

3.2 Extraction of Methylmercury From Sediments

The intractability of methylmercury in the analysis of environmental samples is well known in the literature, and is further evidenced by an almost total absence of certified methods or standard reference materials, despite the intense interest in quantifying this compound in environmental studies around the world.

At the commencement of the analytical work, the method of Donais et al. (1996) was followed for all aspects of the extraction and analysis. However, it quickly became apparent that their results were not easily reproducible. At this point, it was not known whether it was the extraction technique or the instrumentation that was at fault, but the observed detection limit was several orders of magnitude higher what was desired.

As a result, further testing of this and other extraction techniques continued, and in addition, a number of experiments were carried out to determine the reproducibility and accuracy of the analytical techniques employed. Potential losses due to volatility were of particular concern, as extensive handling of relatively small amounts of sample was required. Also, tests were conducted to ensure there was no carryover, or "memory effects" of Hg in the instrumentation from sample to standards to blanks –i.e. that the GC-AED system was thoroughly purged after every injection and analysis.

The difficulties in extracting methylmercury for analysis quickly become apparent when reviewing literature on this topic, in that the techniques used and the results obtained from them are quite variable, and even occasionally contradictory. For example, Horvat et al. (1993) found that while acid extraction of sediments should be favourable because H^+ competes with CH_3Hg^+ for sediment binding sites and prevents hydrolysis of CH_3Hg^+, the least effective method of those they studied was extraction by HCl. Not

even 8M HCl released all CH_3Hg, and in fact was partially decomposed by it in the studies by Horvat et al. (1993). However, Nagase et al. (1980) report excellent recoveries and reproducibility using 2N HCl followed by steam distillation.

Addition of Cu^{2+} should aid in acidic extractions[28] as in the reports by Donais et al. (1996) by competing with CH_3Hg^+ for sediment binding sites, but Horvat et al. (1993) did not obtain quantitative recovery of CH_3Hg. It was not clear in their case whether incomplete digestion or problems with the ethylation derivatization caused their low results.

Horvat et al. (1993) also found that 25%KOH/methanol effectively extracted CH_3Hg^+ from sediments. As per the work of Donais et al. (1996), the KOH/methanol with Cu^+ addition digestion was attempted first, but satisfactory results could not be obtained. Further experiments to develop a satisfactory extraction method are described below.

Bartlett et al. (1977) have even shown that methylation can take place after sediments have been recovered and before analysis, especially if the conditions (pH, Eh, temp, O2) have changed. It is quite possible that the reason for these varying successes with different approaches to the extraction of methylmercury from sediment may be due in part to the varieties of sample matrix that can occur in sediment samples.

3.3 Extraction and Derivatization Procedure for Methylmercury Analysis

3.3.1 Background Developmental Work

The initial starting point for the analytical development carried out on this project was the work published by Donais et al. (1996) at the National Institute of Standards and

Technology, Maryland USA. Their work also centered on a Hewlett-Packard GC-AED system, and was focused on methylmercury determinations in aquatic organisms and sediments. Compared with other literature which used GC-based separations for organomercury analysis, one of their main departures from common practices was to use a shorter capillary column with a much thicker stationary phase (3.0μm), which is uncommon to the point that it is not widely available from many column manufacturers in that particular stationary phase (14% cyanopropyl-86% dimethylsiloxane). However, recent publications show that the use of thicker-filmed capillary columns is gaining acceptance for the study of methylmercury by capillary gas chromatography (Cela-Torrijos et al. 1996). At the time, a similar column could not be obtained from the same manufacturer (Quadrex), but one was purchased with the same specifications from RESTEK (Bellefonte, PA). The work was duplicated as closely as possible but satisfactory detection limits could not be achieved, only solutions >30ug/mL methylmercury would produce quantitative peaks.

Following this, a KOH/methanol extraction was attempted following after the work of Carrichia et al. (1997), again without satisfactory results.

Finally, a method published by Hewlett-Packard application specialists, Frimmel and Gremm (1993) was attempted. This technique involved a Grignard derivatization prior to chromatographic analysis. This step was designed to overcome one of the major problems of chromatography of methylmercury. If methylmercury is extracted using a procedure with low pH followed by back-extraction into an organic solvent, it will typically be present in the solution in the form CH_3-Hg-X, where X is Cl or Br, depending on the reagents present in the acidic extraction.

The problem with this is that the mercury – halide ion bond (Hg – X) is very weak, and can easily dissociate under the higher temperatures within the GC instrument. As a result, the organo-mercury compounds break down in the injector and can then become bound to the column stationary phase resulting in the problems mentioned above. The chromatography of mercury compounds has been the subject of a number of articles and has resulted in a number of solutions such as conditioning the column at regular intervals with solutions containing extremely high concentrations of mercury prior to and interspersed with the analysis of actual samples (Rubi et al. 1994). However, it was decided to avoid this step due to concerns of contaminating the AED system and thus raising the background level of the Hg signal observed.

As a result, the Grignard derivatization technique described by Frimmel and Gremm (1993) was employed, as illustrated in Equation 3-1. The Grignard reaction is widely used in synthetic organic chemistry to join chains of carbon molecules together, and it was employed here to create a dialkyl compound from the extracted methylmercury. The dialkylmercury compounds are much more stable and less likely to break down under the conditions found within the GC system (Bulska et al. 1991).

$$CH_3Hg^+ + CH_3CH_2CH_2CH_2MgBr \rightarrow CH_3Hg(CH_2)_3CH_3$$

Equation 3-1. The Grignard reaction of methylmercury with butylmagnesium bromide in the extraction procedure, producing methylbutylmercury.

3.3.2. Analytical Method for Methylmercury Determination

- 10g each of wet sediment was weighed into two (one sample, one spiked sample) 50mL centrifuge tubes. At this time, two tubes were also set aside for a Method Spike and Reagent Blank as well.
- 1mL of 20pg/uL ethylmercury chloride in methanol was added to each sample, spiked sample, and to the Method Spike.
- 1mL of 200pg/uL methylmercury chloride in methanol was added to each of the sample spikes and the Method Spike.
- 10mL of 1N HCl (environmental grade) was added to each tube. They were swirled to ensure thorough mixing, and allowed to stand in a fume hood for two hours in case any H_2S was produced.
- Following this, the tubes were agitated for 20 minutes in an ultrasonic bath at room temperature, and then centrifuged for three minutes to settle out the suspended sediment.
- The supernatant liquid was decanted into clean 50mL centrifuge tubes.
- The acid digestion and ultrasonic steps were repeated twice, and the supernatant phases were combined.
- 1mL of 2% dithizone (diphenylthiocarbazone) in methanol was added to each extracted sample, after which they were swirled and placed in the ultrasonic bath for 10 minutes.

- 4mL of toluene (Caledon, pesticide grade) was added to each tube which was then shaken by hand and allowed to stand for 20 minutes –a complex emulsion usually formed at this point, making extraction of the organic phase difficult.
- Disposable pipettes were used to extract the toluene layer into 15mL disposable glass centrifuge tubes, which had been calibrated to 1.0mL.
- The dithizone, ultrasonic, and toluene steps were repeated twice more, and the resulting 12mL of sample was concentrated down to 1mL using a water bath / N_2 stream.
- The toluene solution was dried by passing it over Na_2SO_4 (in a pipette) into a clean test tube.
- The Na_2SO_4 was rinsed with a further 1mL of toluene.
- 0.5mL of 1.0M butylmagnesium chloride in tetrahydrofuran Grignard reagent (Aldrich) was added to each sample and they were shaken and left to stand for 30 minutes.
- Also at this time, a set of calibration standards was prepared using 1mL of 1, 5, 10, 50, 100, 500, 1000pg/uL mixed organomercury standards in toluene (each contained methyl-, ethyl-, and phenylmercury chloride –obtained from Alfa AESAR, Ward Hill MA).
- 2mL of 1N HCl was added to 'quench' the reaction, and then the upper (non-aqueous) layer was extracted and passed over Na_2SO_4 into a clean test tube.
- These solutions were then transferred into GC autosampler vials and run on the GC-AED.

3.4 GC-AED Instrument Operating Conditions

3.4.1 GC conditions

Column / Transfer Line:	Hiresco OV-1 XL, (P/N HI-1150/180) 30 m, 0.25 mm ID, 0.25 μm film thickness
Column Head Pressure:	Helium, 16 psig
Injector:	Split/Splitless (Splitless Mode)
Injection Size:	2 uL
Injector Temperature:	230° C
Injector Purge Time:	(off) 1.00 min

3.4.2 GC Temperature Program

0.5 min @ 80° C, 45 C° / min to 230° C, 5 min hold @ 230° C

3.4.3 AED Instrument Conditions

Analytical Wavelength:	254 nm (nominal)
Oxygen Flow:	4.92 mL/min
Hydrogen Flow:	4.39 mL/min
Helium Make-Up flow:	22 mL / min
"High" Helium Make-Up Flow:	not used
Solvent Vent Time:	3.25 min
Spectrometer Purge Flow:	Nitrogen (~0.5L/min)
Cavity Temperature:	230° C
Transfer Line Temperature:	230° C
Cavity Pressure:	13 psig (1.9 kPa)

The AED was operated under low-flow conditions (low Hydrogen, Oxygen and Helium Makeup flow) which served to optimise Hg sensitivity and to have little effect on chromatographic performance (peak shape). The software methods were designated as ~HGNOSPEC.m and ~HGSPEC.m, denoting whether spectral data was recorded or not. Spectra were not collected for the standards or wash solutions.

3.5 Data Processing of GC-AED Results

All primary data processing was done using the instrument control software, Hewlett-Packard GC-AED ChemStation (Rev.# A.03.04 for MS-Windows™ 3.11) to provide background interference corrections and peak area integration. The main interferences in these spectra were of a background broadband "continuum" nature, caused by emission spectra of the large amount of carbon present –in severe cases this would impart a bright green colour to the normally blue-white helium plasma. This was corrected by using algorithms prewritten into the AED software, which would remove extraneous signal noise from the chromatograms by applying a background correction factor. In most cases the software would apply the correction value automatically, but this was also done manually for a number of samples on the advice of instrument software engineers, in cases where the algorithms introduced significant peak distortion. When done manually, the correction factor was increased to the largest value possible while still maintaining symmetrical peak shape/baseline attributes. All the standard and sample spectra were then integrated using manually selected points.

Once this had been completed all remaining calculations were done using a spreadsheet. First, the responses for the methylmercury peaks in the mixed standards were plotted, and the slope was calculated, to determine the instrument's sensitivity (counts/pg) to mercury at a given point in time, in case this varied over the course of a run, or during successive runs. Since standards were measured at the beginning, middle, and end of every run, these results were interpolated to approximate the sensitivity at the actual moment when each sample or spike was measured.

Using the technique of 'known additions', the following steps were carried out;

- The absolute responses for a given sample and its spike were determined.
- The response for a spiked sample was corrected for the presence of any methylmercury in the unspiked sample.
- The sensitivity was then determined for methylmercury by dividing the nominal spike concentration by the absolute mercury response (e.g. 200pg/uL by 200 count/sec).
- The methylmercury response for the 'unspiked' sample was then multiplied by this sensitivity to give the concentration present in the sample.
- This value was then corrected for the final volume of analyzed concentrate, the raw (wet) sample weight, and the moisture content of the sample.

3.6 Analytical Development Results

The main goal in the development of this analytical method was to devise a robust technique that would provide quantitative separation of organomercury

compounds from the sample matrix, as well as provide confirmation that the specific analyte desired had been measured. As has been shown, these goals are not always possible with other techniques and apparatus. The combination of capillary gas chromatography and microwave plasma ionisation-atomic emission detection, however, does meet these objectives.

As can be seen in Figure 3-5 the desired separation was achieved, with the peaks of various organomercury compounds being clearly resolved even at very low concentrations over a very short analytical time frame. The GC-AED system was capable of recording 'snapshots' of the spectral wavelength window being measured, at a rate of five scans per second, and these were used to confirm the presence of mercury within a selected chromatographic peak (Figure 3-6).

Once the basic suitability of the instrumentation had been demonstrated, the next step was to determine the sensitivity and response of the detector over a wide dynamic range. This was done using a set of standard solutions, which were prepared to concentrations of 1, 5, 10, 50, 100, 500, and 1000 pg/uL of methylmercury (as Hg). These standards were run at the beginning, middle, and end of each analytical run, in order to observe sensitivity and to provide an indicator of any potential problems. The results of these analyses have been tabulated for four different analytical sequences from March 18-26, as seen in Figure 3-7.

In addition to demonstrating the stability and reproducibility of the GC-AED instrumentation, it is also important to note that these results concomitantly demonstrate the reproducibility of the Grignard derivatization step itself. This was seen as a key validation of the techniques used, and it is hoped that once the actual extraction yields

from the sediment steps have been improved further, the overall technique will have greatly increased applicability.

Having established reproducible instrumental performance, the efficiency of the extraction and derivatization steps was also determined. This was done using two approaches; 1) the use of method spikes, which were reagent blanks that had been spiked with methylmercury, and 2) sample spikes, in which a sub-sample of each portion of sediment analysed was also spiked with methylmercury. The method spikes enabled the efficiency of 1) the extraction from the aqueous phase into the toluene and 2) the Grignard derivatization to be determined. These two factors combined had an overall mean efficiency of 67% (Figure 3-8).

Following from this, the efficiency of the extraction for the actual samples was determined. Although all the samples were collected from the same general area, they still consisted of highly variable matrices, particularly with regard to sand, clay, silt, and organic content. As a result, it was decided to analyse a spike of every individual sample, in order to account better for this variability. These spikes had a consistent, but much lower, average recovery of 22% (Figure 3-9).

Finally, the reproducibility of the extractions was calculated using the ethylmercury internal spikes as duplicates for each of the samples in lieu of any certified reference materials for methylmercury. The average reproducibility of all of these analyses was ± 25%. This technique was used in order to approximate the accuracy of methylmercury analysis using this method given the close chemical similarity between these compounds.

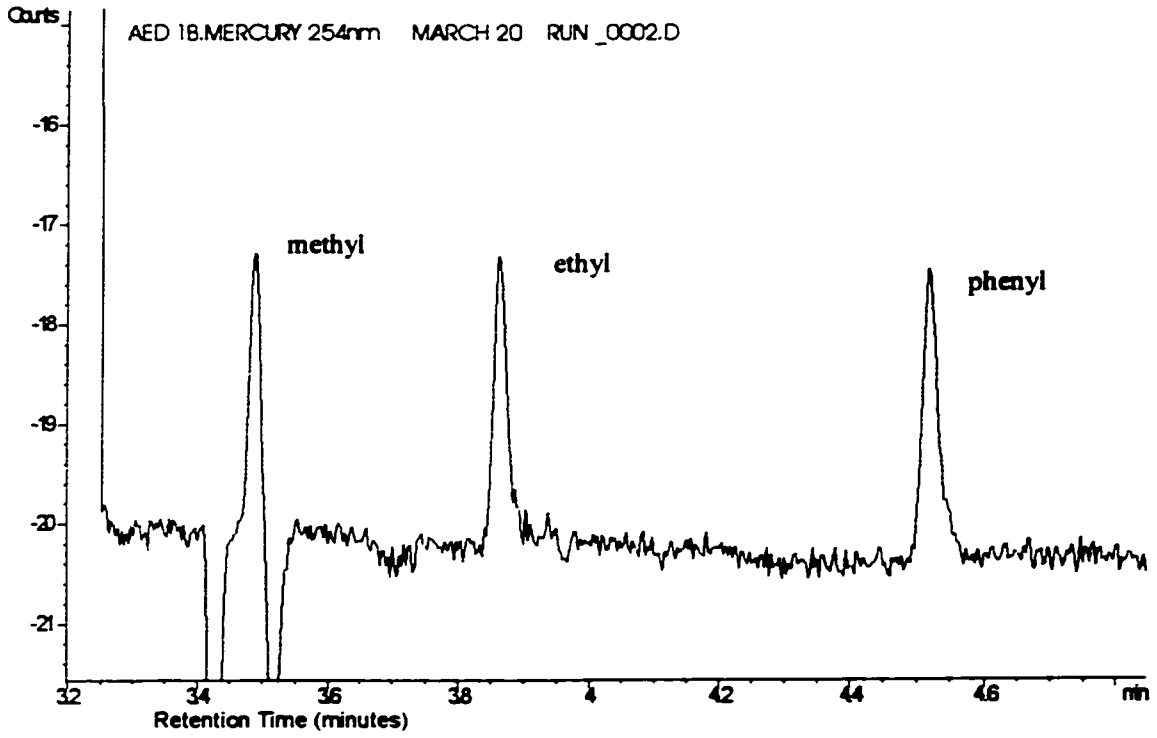

Figure 3-5. A chromatogram of counts (X-axis) vs. retention time (Y-axis) of an analytical separation of a 1pg/uL mixed organomercury standard containing methyl-, ethyl-, and phenyl-mercury. The negative numbers on the Y-axis are an artefact of the algorithms used in the baseline interference corrections.

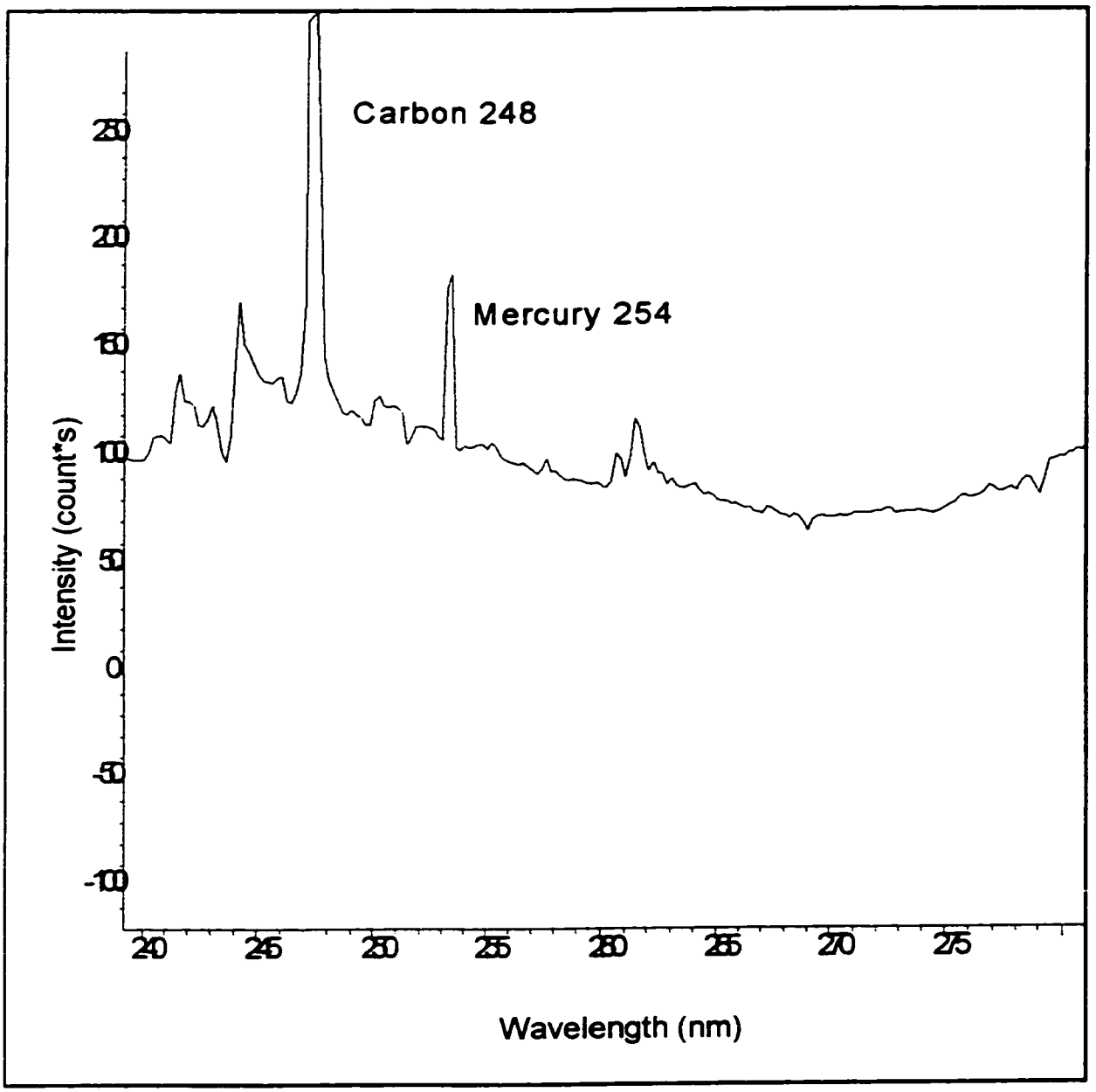

Figure 3-6. An example of a spectra from a mercury-containing chromatographic peak.

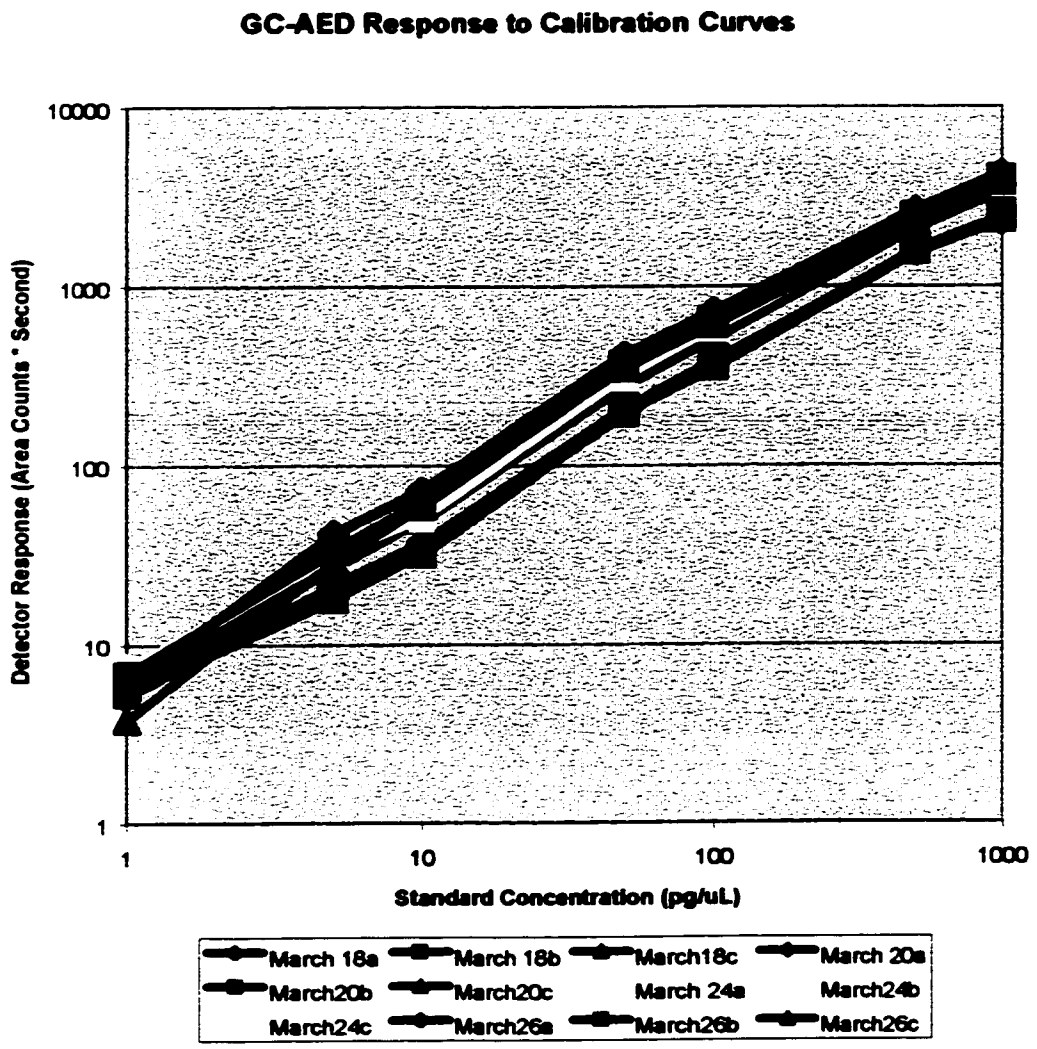

Figure 3-7. Calibration curve response for four consecutive analytical runs, showing integrated response in area counts*s (Y-axis) vs. concentration of the standard solutions (X-axis).

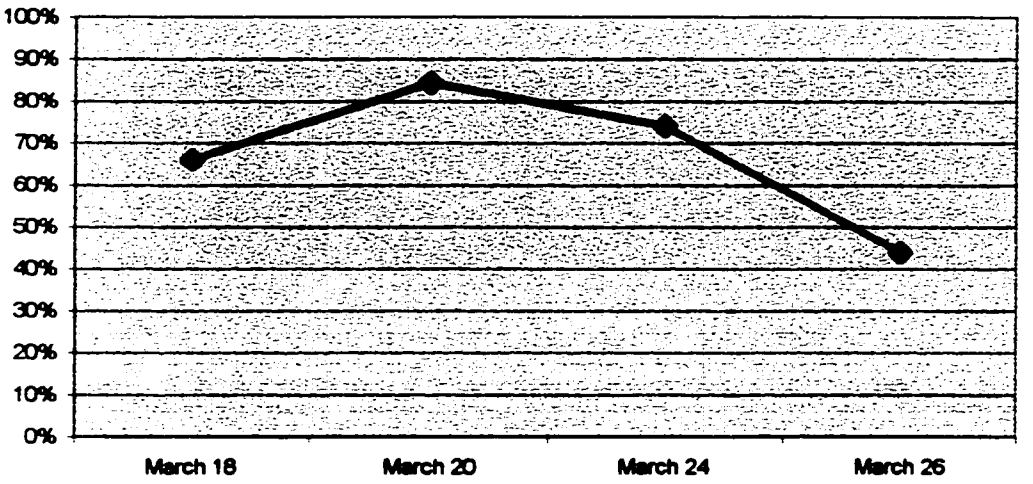

Figure 3-8. Recovery (expressed as a percentage) of the Method Spike samples (spiked blanks) for each of the four analytical runs.

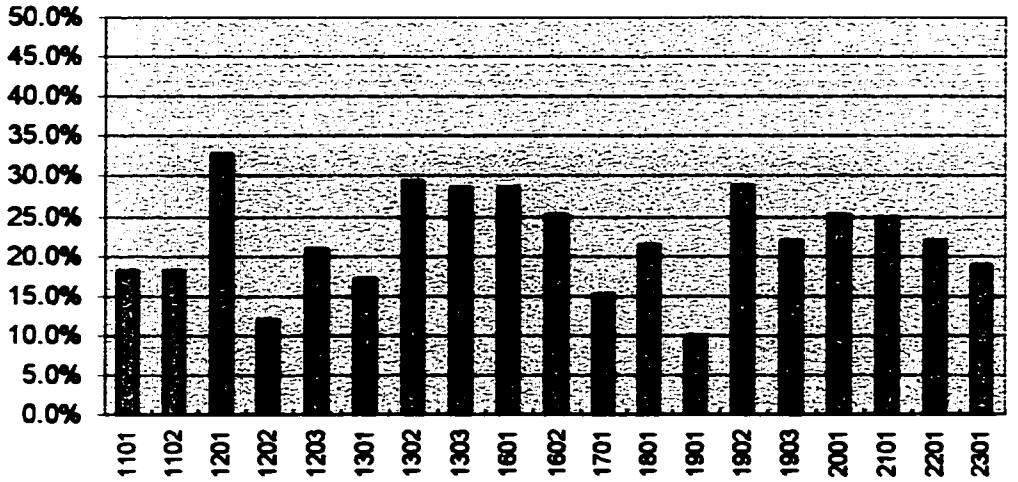

Figure 3-9. Recoveries of methylmercury from spiked sediment samples. The codes on the X-axis identify the actual sample locations and sub-samples for each respective site, as described previously.

CHAPTER FOUR

RESULTS

4.1 Introduction

The results of the analytical work for this project reveal a number of interesting facts about the current state of mercury contamination in the sediments of Lake St. Clair. Inorganic mercury is still present in elevated levels at a number of sites across the lake basin, and is still significantly high at one location. It is believed that this is the first project ever done on Lake St. Clair sediments for methylmercury, since no previously published results could be found. Methylmercury was found at a number of locations, but not every site that had high total mercury had correspondingly elevated methylmercury concentrations.

4.2 Analytical Results: Total Mercury

In addition to the methylmercury determinations described in Chapter 3, all the sediment samples were tested for total mercury content to determine in what proportion the methylmercury was in comparison with the overall total mercury concentration. As discussed in Chapter Two, this was done using flameless atomic absorption.

The results of this total mercury work are given below in Table 4-1A and 4-1B for the smaller cores, and the results from the large core from the LIMNOS are given in Table 4-2. The maximum mercury concentration (dry weight corrected) measured was 0.906 ug/g, and the average concentration was 0.130 ug/g. The mercury concentration in

the sediments was not evenly distributed throughout the lake, but instead showed one localised "hot spot" at Site #1 (Belle River) shown in Figure 4-1 and all of the other locations had much lower levels. Results from several of the deeper cores (>20cm) at Sites #3, #8, and #12 from around the lake can be seen in Figures 4-2 through 4-4. In the core taken aboard the LIMNOS, shown in Figure 4-5, it can be seen that even though the overall mercury levels at this location are several orders of magnitude lower than those seen at some other sites, there is still a clearly visible "spike" just below the sediment-water interface before concentrations decline into the background levels of the underlying glacial clays.

Most of the deeper cores (including the large core taken aboard the LIMNOS) showed that the levels of contamination were highest at or near the sediment-water interface, and in most cases dropped off rapidly with increasing depth. The exception to this is the core at Site #1, where the zone of maximum mercury concentration occurs 10-15cm below the sediment surface, and to a lesser degree at site #12 where the maximum concentration occurs at 5-10cm depth. Historical data for the same area of the lake is available in the paper by Mudroch et al. (1989) for core samples taken in 1985. The data for Site #1 of the present study is plotted with data from site #18 from the 1985 survey, which corresponds to approximately the same location, shown in Figure 4-6. It is apparent that the zone of maximum mercury concentration now occurs approximately 5cm deeper than it did 12 years previously. Since, as was previously stated, Lake St. Clair is considered to be a "non-depositional environment", it is unlikely that 5cm of sediment accumulation has taken place in little over a decade. Therefore, it is postulated that some

other diagenetic processes may be a factor. However, further data collection would be required to provide a clearer answer to this question.

4.3 Methylmercury Results for Lake St. Clair Samples

Once all the sediment samples had been analysed for total mercury content, the analysis for methylmercury was carried out. It was decided to only perform the extraction and analysis on samples that had in excess of 0.04 ug/g total mercury. This was based on preliminary experiments which had already indicated the sensitivity and efficiency of the methylmercury technique, as previously shown in Figures 3-8 and 3-9. Other literature reports, for example Watras et al. (1994), showed that methylmercury in sediments occurred at c.a. 1-3% of the abundance of total mercury, and therefore concentrations lower than this (in this case, 0.0004 ug/g) were not likely to be observable with the present extraction method based on a nominal detection limit of 0.001 ug/g.

The results of the methylmercury analyses are shown in TABLE 4-2, which presents the background correction applied (used to correct for spectral interferences) the retention time of the methylmercury peak, the area under the peak (determined by manual integration) and the calculated results for the methylmercury concentration.

The methylmercury and total mercury results for all of the sites which had measurable amounts of methylmercury, are shown in Table 4-3 and Figure 4-7. The mean proportion of methylmercury to total mercury is 1.01%, which agrees well with the

literature, as mentioned previously. However, at this time there is no information to indicate why one sample, #12-02 is an order of magnitude higher than in all of the others.

Site ID-Codes	Depth in Sediment (cm)	Dry Hg (ug/g)	Moisture (%)
ATC-01	5	0.648	37.3
ATC-01	10	0.552	36.4
ATC-01	15	0.906	34.0
ATC-01	20	0.146	27.4
ATC-03	5	0.048	22.6
ATC-03	10	0.021	27.4
ATC-03	15	0.017	26.7
ATC-03	20	0.018	28.3
ATC-03	25	0.018	27.0
ATC-04	5	0.029	23.8
ATC-05	5	0.016	25.7
ATC-05	10	0.013	26.5
ATC-06	5	0.033	21.8
ATC-06	10	0.019	21.7
ATC-07	5	0.151	26.9
ATC-07	10	0.238	33.3
ATC-08	5	0.028	29.6
ATC-08	10	0.020	38.7
ATC-08	15	0.022	37.4
ATC-08	20	0.021	39.3
ATC-08	25	0.021	37.0
ATC-09	5	0.055	22.7
ATC-10	5	0.067	28.5
ATC-10	10	0.105	25.4

Table 4-1a. Total mercury results for Lake St. Clair sediment samples showing the site number, depth interval, total mercury in ug/g, and moisture content. Detection limit was 0.002 ug/g.

Site ID Codes	Depth in Sediment (cm)	Dry Hg (ug/g)	Moisture (%)
ATC-11	5	0.068	28.2
ATC-11	10	0.146	33.0
ATC-12	5	0.08	23.6
ATC-12	10	0.207	23.2
ATC-12	15	0.078	22.5
ATC-12	20	0.016	22.6
ATC-12	25	0.025	24.2
ATC-13	5	0.068	30.9
ATC-13	10	0.085	27.7
ATC-13	15	0.174	24.1
ATC-14	5	0.033	23.6
ATC-14	10	0.036	24.3
ATC-15	5	0.02	29.6
ATC-16	5	0.079	28.5
ATC-16	10	0.102	25.5
ATC-17	5	0.06	26.6
ATC-18	5	0.055	26.2
ATC-18	10	0.044	25.0
ATC-19	5	0.066	36.2
ATC-19	10	0.073	33.1
ATC-19	15	0.06	30.0
ATC-20	5	0.017	22.1
ATC-21	5	0.122	24.8
ATC-22	5	0.132	21.0
ATC-23	5	0.103	24.4
ATC-23	10	0.04	20.0

Table 4-1b. Total mercury results for Lake St. Clair sediment samples (continued).

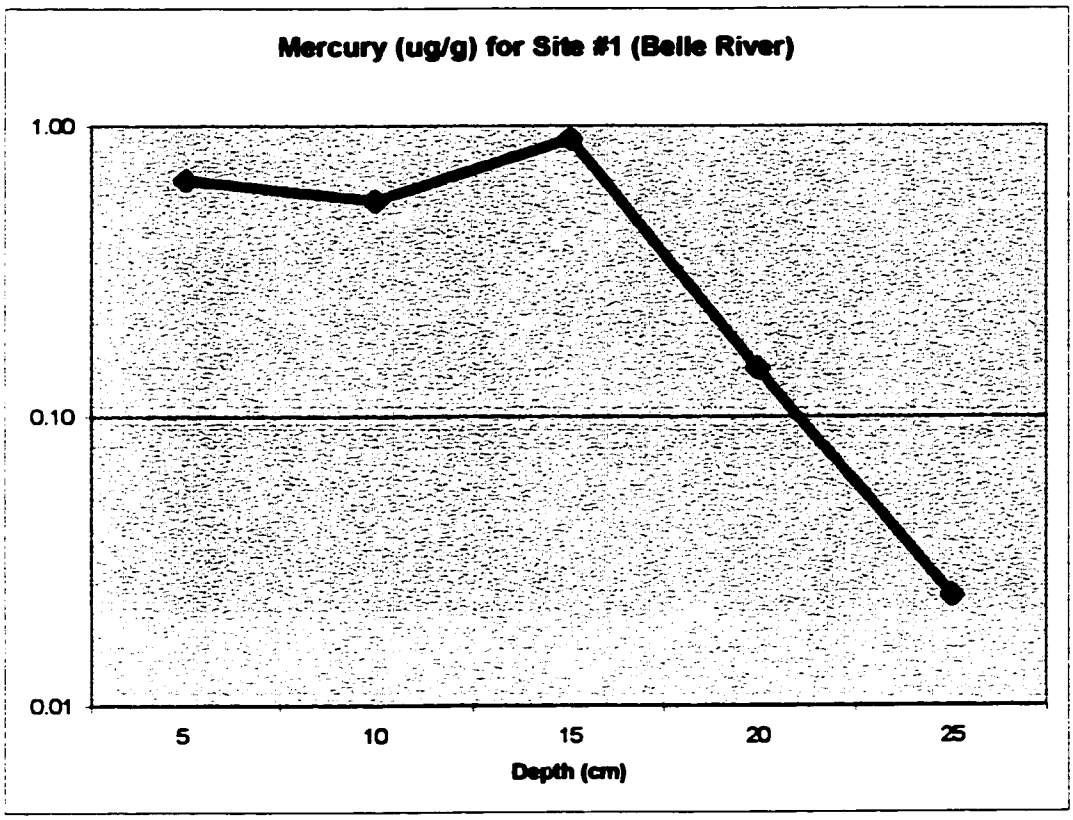

Figure 4-1. Total mercury concentrations for Site #1 in ug/g.

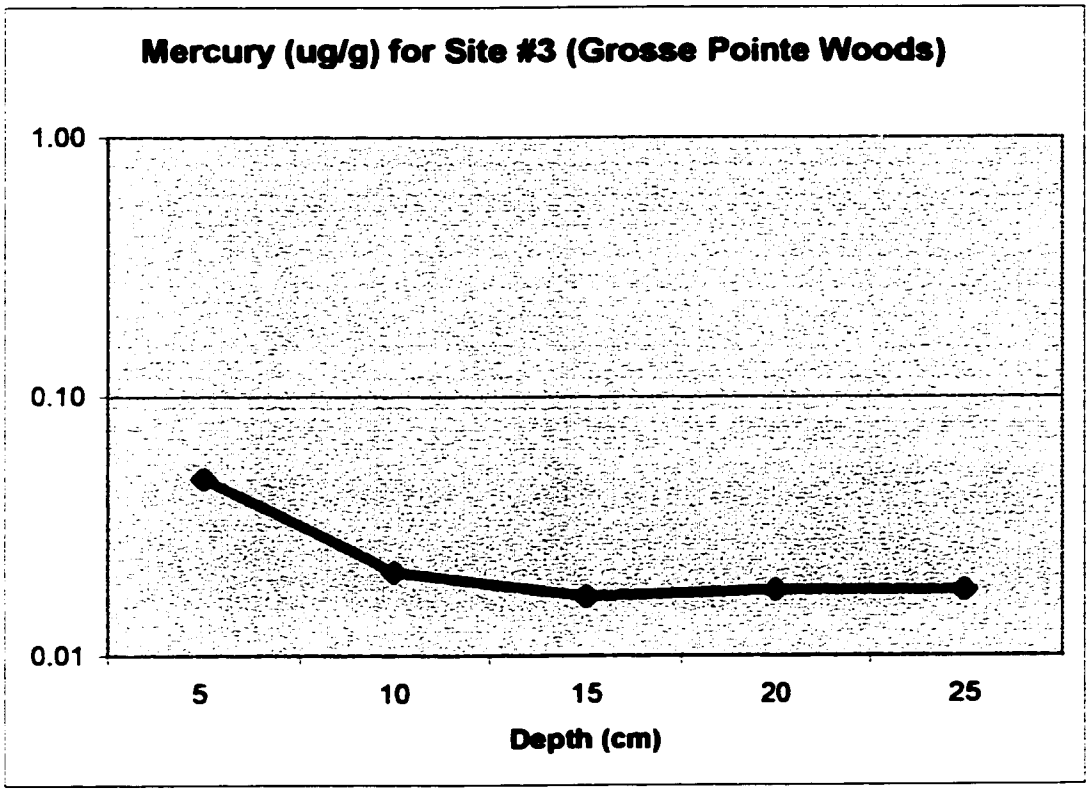

Figure 4-2. Total mercury concentrations for Site #3 in ug/g.

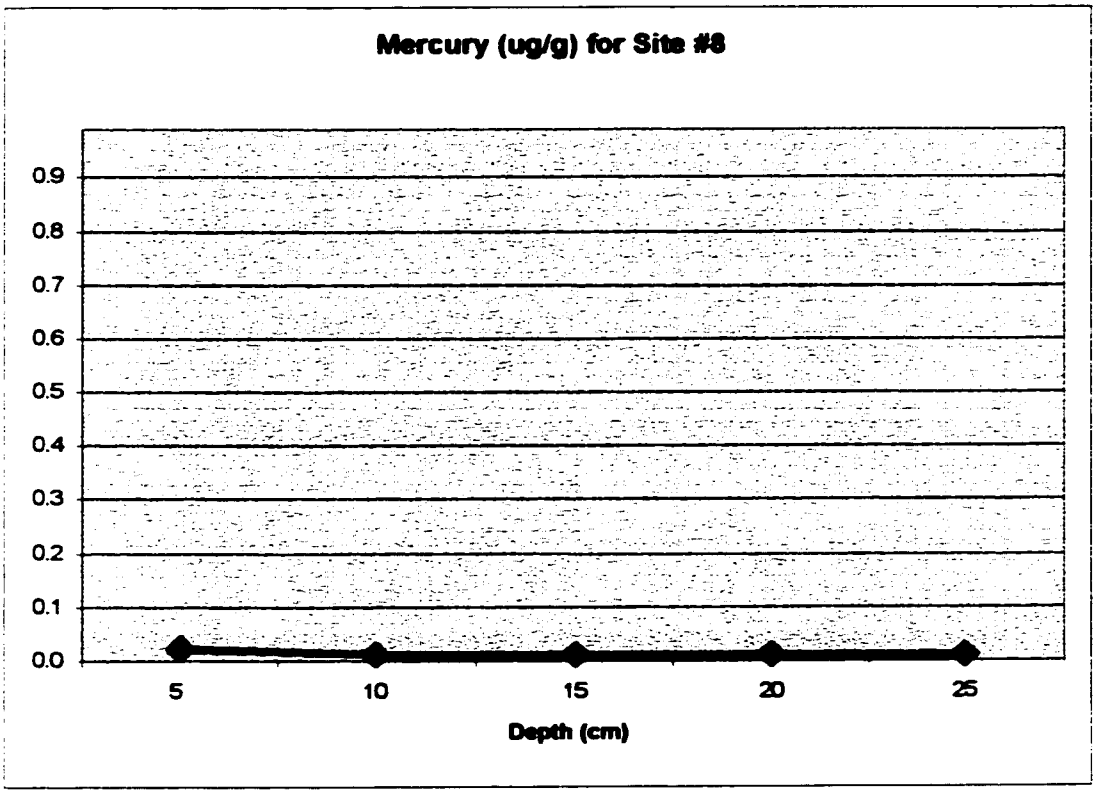

Figure 4-3. Total mercury concentration for Site #8 in ug/g.

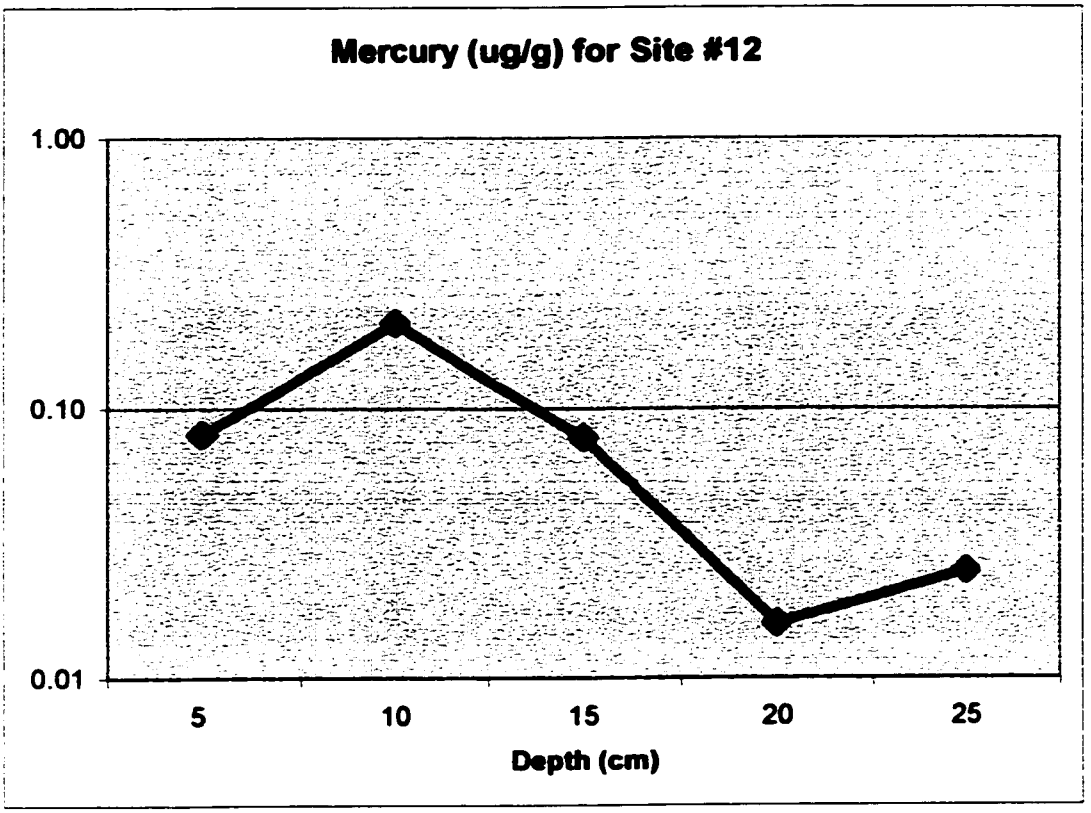

Figure 4-4. Total mercury concentrations for Site #12 in ug/g.

Depth (cm)	Mercury (ug/g)	Moisture
0-2	0.041	30.4%
2-4	0.057	22.9%
4-6	0.045	26.3%
6-8	0.017	20.2%
8-10	0.015	21.1%
10-11	0.021	28.5%
11-12	0.016	28.2%
12-13	0.014	28.2%
13-14	0.014	28.1%
14-15	0.015	29.3%
15-16	0.016	30.2%
16-17	0.013	33.7%
17-18	0.014	32.6%
18-19	0.012	34.7%
19-20	0.014	33.9%
20-21	0.015	33.6%
21-22	0.015	31.1%
22-23	0.015	33.2%
23-24	0.018	29.6%
24-25	0.016	28.0%
25-26	0.014	29.2%
26-27	0.014	30.8%
27-28	0.016	28.8%
28-29	0.015	29.0%
29-30	0.016	30.7%
30-31	0.014	31.5%
31-31.5	0.015	31.2%

Table 4-2. Total mercury and moisture content for the core taken aboard the LIMNOS at Site #21. Detection limit was 0.002 ug/g.

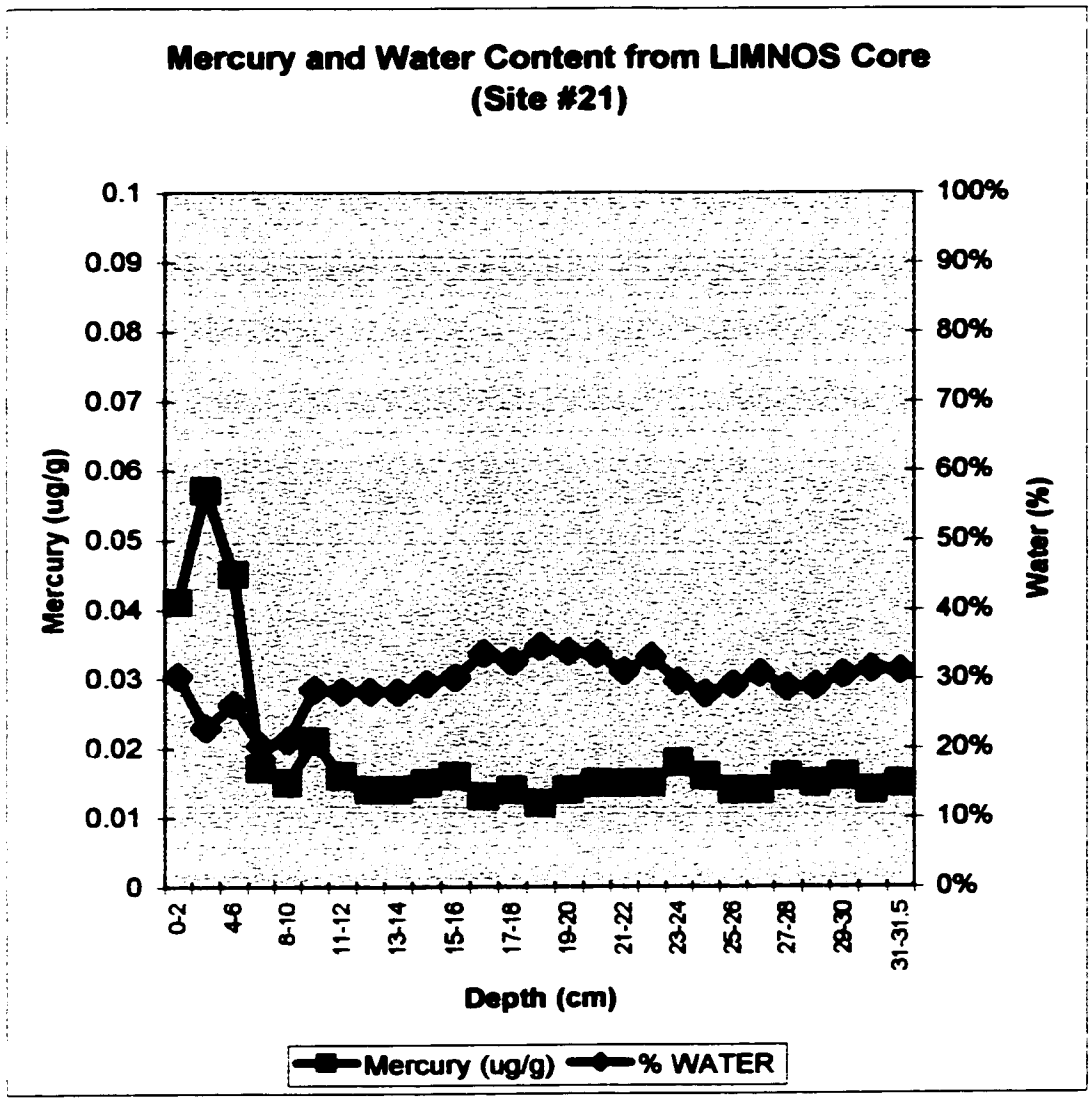

Figure 4-5. Total mercury concentrations for Site #21 (LIMNOS core)

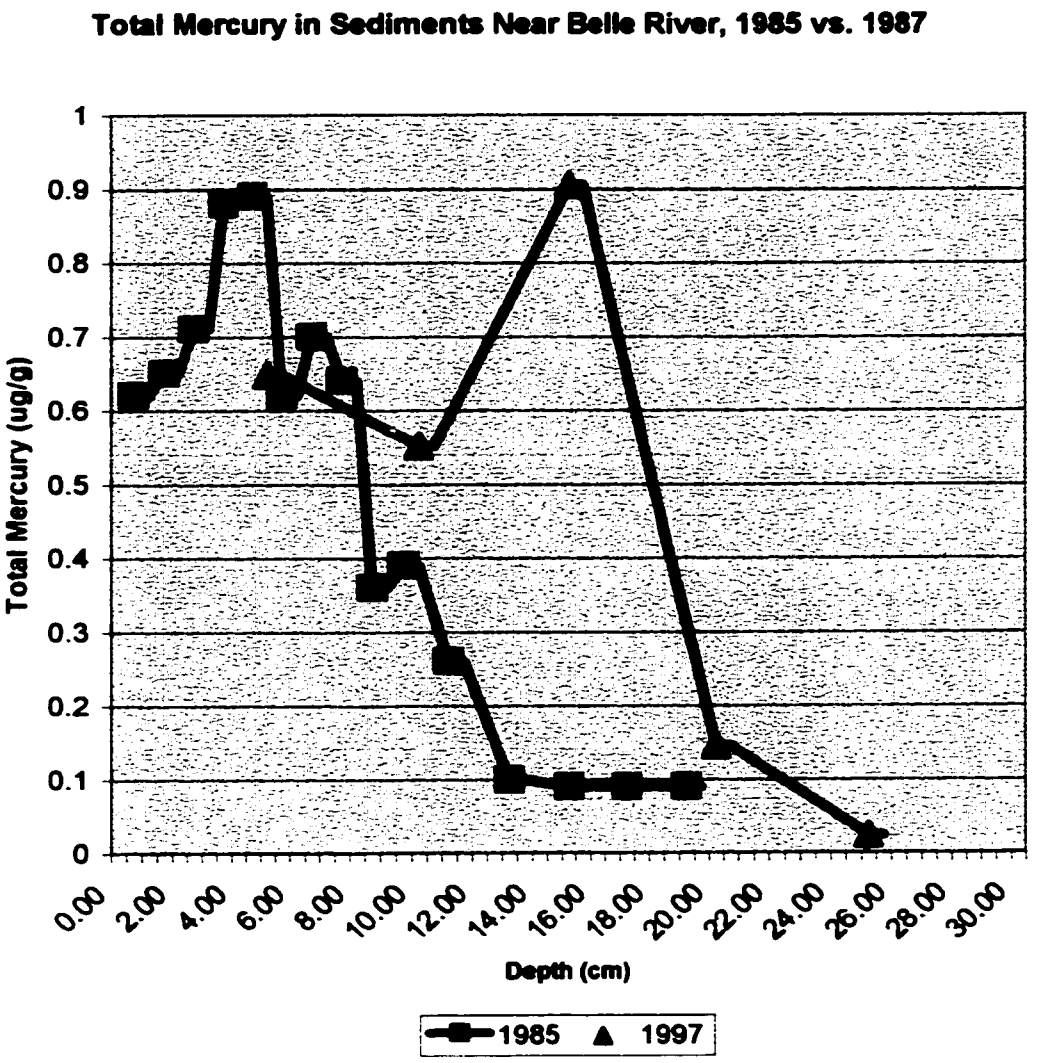

Figure 4-6. Total mercury concentrations for Belle River location (Site #1, present study) compared with results from a previous sediment survey. (Mudroch et al. 1989)

Site ID#	Background Correction	Retention Time (min)	Peak Area (Area Counts*s)	Methylmercury (ng/g dry weight)
01-01	0.85	3.472	1.14	0.41
01-02	0.86	3.46	0.67	0.03
01-03	ND	ND	ND	ND
01-04	ND	ND	ND	ND
07-01	0.8	3.453	6.89	0.24
07-02	0.82	3.461	5.34	0.15
09-01	ND	ND	ND	ND
10-01	0.85	3.463	0.90	0.04
10-02	ND	ND	ND	ND
11-01	1.13	3.538	3.27	0.85
11-02	1.10	3.513	2.36	0.69
12-01	1.12	3.52	2.43	0.35
12-02	1.08	3.509	61.98	17.37
12-03	1.09	3.512	4.75	1.53
13-02	1.12	3.528	2.42	0.31
13-03	1.13	3.533	0.69	0.08
16-01	1.12	3.529	2.56	0.33
16-02	0.82	3.511	3.15	0.46
17-01	0.85	3.537	1.55	0.34
18-01	0.83	3.517	1.38	0.21
19-01	0.82	3.515	1.86	0.79
19-02	0.82	ND	ND	ND
19-03	0.81	ND	ND	ND
20-01	0.87	ND	ND	ND
21-01	0.86	3.549	6.13	2.17
22-01	0.84	3.553	4.44	1.92
23-01	0.84	3.558	1.24	0.61
			MEAN	**1.39**

Table 4-3. Methylmercury Results from GC-AED Analysis of Lake St. Clair Sediments. "ND" indicates insufficient peak height for quantitation. Detection limit is 0.01 ng/g in sediment.

Site Code	Methylmercury (ng/g)	Total Mercury (ng/g)	Proportion of methyl- to total Hg
01-01	0.41	648	0.06%
01-02	0.03	552	0.01%
07-01	0.24	151	0.16%
07-02	0.15	238	0.06%
10-01	0.04	67	0.06%
11-01	0.85	68	1.25%
11-02	0.69	146	0.48%
12-01	0.35	80	0.44%
12-02	17.37	207	8.39%
12-03	1.53	78	1.96%
13-02	0.31	85	0.37%
13-03	0.08	174	0.05%
16-01	0.33	79	0.42%
16-02	0.46	102	0.45%
17-01	0.34	60	0.57%
18-01	0.21	55	0.39%
19-01	0.79	66	1.20%
21-01	2.17	122	1.78%
22-01	1.92	132	1.45%
23-01	0.61	103	0.59%
MEAN	**1.45**	**161**	**1.01%**

Table 4-4. Methylmercury and Total Mercury Relative Abundances from Lake St. Clair Sediments.

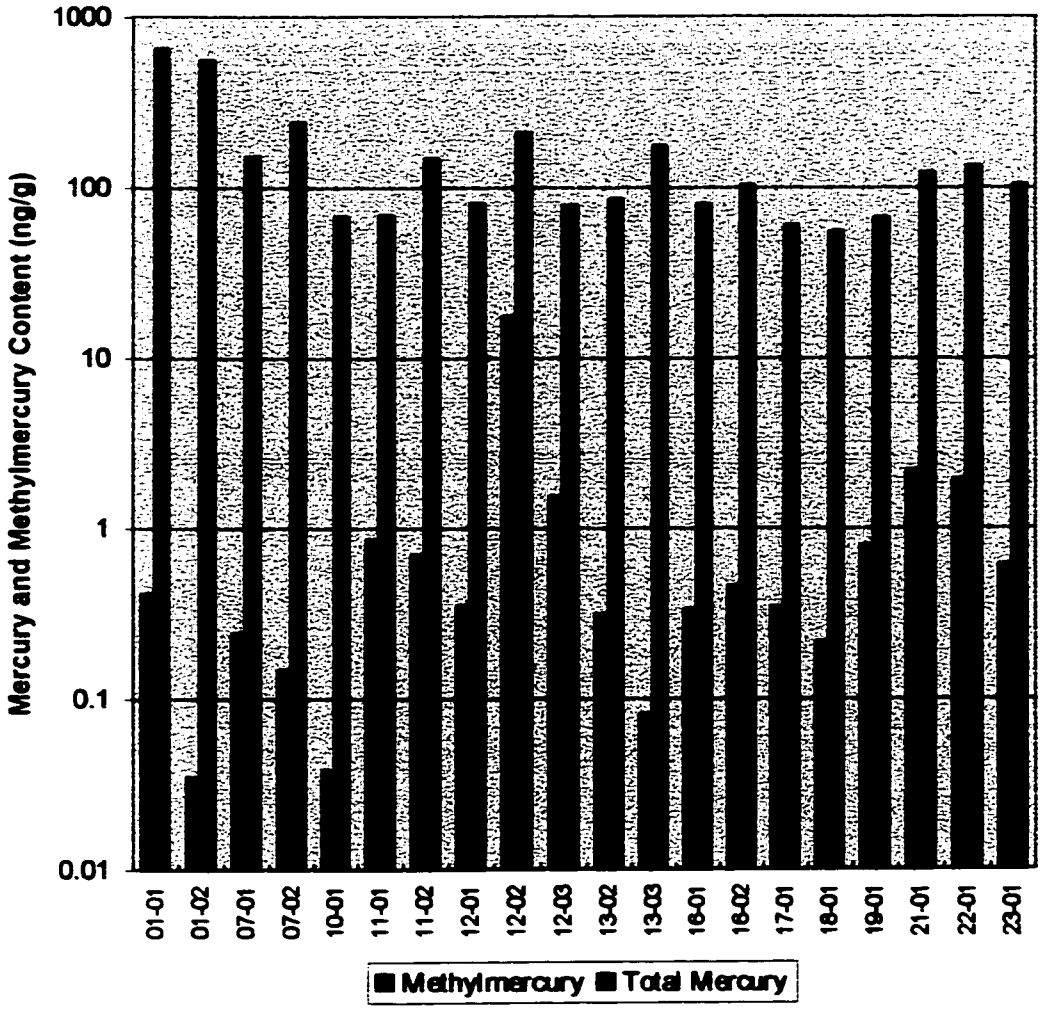

Figure 4-7. Total mercury and methylmercury for all samples found to contain methylmercury in Lake St. Clair plotted with their site location and depth codes. The unusually high concentration of methylmercury in Site 12-02 is clearly visible.

CHAPTER FIVE

DISCUSSION

5.1 Methylmercury Analysis Techniques

The methylmercury analysis technique developed for this thesis was based on and modified from a number of different techniques in the literature. It is well established that the analysis of methylmercury is not a straightforward task, and that has certainly proved to be the case in this project. However, it should be noted that the instrumental apparatus and technique performed satisfactorily, yielding good stability and detection limits. The extraction of methylmercury from the sediment, on the other hand, is still not optimal, and this is usually the limiting step that makes methylmercury analysis so difficult. If this could be overcome, the GC-AED technique looks very promising, for providing quantitative results at even lower levels for environmental samples.

5.2 Total Mercury Results for Lake St. Clair

The sediments of Lake St. Clair have been tested extensively in the past for total mercury content, especially during the 1970's and early 80's – given that this lake was one of the first lakes in Ontario where mercury contamination was discovered to be a problem. In fact it was mainly due to the Hg loadings found in Lake St. Clair that the Ontario government initiated a province-wide sport fish monitoring program for mercury.

No published results have been found for the sediments for any time after 1985. Thus, in addition to the methylmercury work carried out here, the present study can also serve to establish a new benchmark for how much the system has changed over the last 13 years. The historical data obtained unfortunately does not give actual numerical values for the maximum concentrations obtained, but instead shows the results as topological plots, with the maximum zone of concentration given as >3 ug/g.

We can still see, however, that the levels of Hg in the sediment have decreased significantly over this interval, although the area of highest concentration or "hot spot" is still seen in the same locality, in the southwestern corner of the basin. Interestingly, despite having a maximum mercury concentration of 905 ng/g, this particular location (Site #1, Figure 2-1) has very little methylmercury, and the sub-sample with the highest total mercury content (10-15cm depth) showed no methylmercury at all. Further, there are preliminary indications that the zone of peak concentration now occurs about ~5cm deeper than the maximum reported for the same area in 1985 (Figure 4-6) as discussed in Chapter Four. Unfortunately, we do not have sufficient data to indicate whether this is a result of sedimentation and burial alone or whether other processes may be at work. Further testing of this locality would perhaps shed some light on this question, especially given that burial by sedimentation is unlikely based on previously reported sedimentation rates. At the same time however, the post-burial diagenetic behaviour of mercury in sediments in general is also a poorly understood process (Gottgens et al. 1999).

The results of the large core from the LIMNOS (Figure 4-5) illustrate two other key points. Even at relatively low total Hg levels, it can be seen that there is a clear "spike" in the concentrations found at and just below the sediment-water interface (0-

6cm). These data also indicate that the Hg contamination in this lake appears to be solely due to recent anthropogenic factors, as opposed to any long-term natural sources such that mercury would be found to permeate the sediments more extensively. It should be noted that in some lakes that exhibit much lower (but still significant) mercury levels than Lake St. Clair, the source of mercury is a matter of some debate when it is not directly attributable to a point source. The debate hinges around whether the mercury is due to atmospheric deposition or to geological processes, both of which will be discussed in more detail below (Friske et al. 1995).

The moisture content data were also reported in the total mercury results (Tables 4-1, 4-2) in this table to illustrate that the water content of the sediment column overall was quite consistent, and therefore should not be a significant factor in the Hg concentrations found at or near the interface.

According to the *Canadian Sediment Quality Guidelines for Mercury* (Environment Canada, 1997) as quoted in Rasmussen et al. (1998) the "threshold effect level" for freshwater sediment is 174 ng/g (dry weight). The threshold effect level is defined as the concentration below which toxicological effects are expected to occur infrequently. The same guideline also indicates a "probable effect level" of 486 ng/g, which represents the concentration of Hg above which toxicological effects are expected to occur frequently. Based on these guidelines then, at least one area in Lake St. Clair still contains mercury levels high enough to be of concern. Interestingly, there was no reference made to methylmercury in these guidelines, despite the fact that this is the compound that actually has the toxicological effects.

Mercury contamination of the Lake Huron – Lake Erie corridor is still of concern to the ecosystem nearly thirty years after the major influx was halted. Of all the sport fish consumption guidelines issued for this region, 60% of them are due to mercury alone (Ontario Ministry of the Environment, 1999).

5.3 Methylmercury Results for Lake St. Clair

The data from the methylmercury analysis, in Table 4-3, shows that most of the sites tested for methylmercury have a fairly uniform methylmercury concentration, with only a few exceptions. This is somewhat contradictory to what was originally expected – that sites in and around the delta of the St. Clair River would show significantly elevated concentrations. Particularly with the large areas of marshland and standing water in the many bays and lagoons, it was thought that the delta environment would be a prime location for the methylation of inorganic mercury. This in turn was also related to another theory; that the sediments in the delta had been acting as a "sink" for mercury when the original influx was taking place from upriver sources. Now that these influxes had been eliminated, and concentrations in the water/suspended sediment column had declined, the delta region would now have higher Hg levels than the water passing through/over it, and would in effect re-release this 'stored' mercury, acting as a new, lower-level source to the ecosystem.

These theories were borne out to some degree by the data obtained in this study, since most of the sites with measurable methylmercury concentrations were in fact found in and around the delta.

However, there still remains no explanation for the fact that the location with the highest inorganic mercury contains little to no methylmercury at all. One possible explanation for this is that the peak concentration is at such a depth (10-15cm) that it is too far removed from the water-sediment interface for the microbial methylation to take place. However, there is still no clear reason how this large a concentration of mercury accumulated this far beneath the surface of the sediment in the first place, and a more thorough investigation of this locality is needed.

5.4 Mercury in Levels in Fish in the Huron-Erie Corridor

Mercury tops the United States' Environmental Protection Agency (EPA) list of 67 contaminants as the air toxic with the greatest public health concern (Cooney, 1998). In a report to the U.S. Congress in December of 1997, the EPA reported they found "evidence for a plausible link between the emissions of mercury from utilities and the methylmercury found in soil, water, air, and fish." However, because of the uncertainties related to environmental fate and transport of mercury, the EPA cannot clearly link fish contamination to mercury emissions (Cooney, 1998).

In addition to all the sediment collection and analysis used for this study, data was also obtained from the Sport Fish Contaminant Monitoring Program of the Ontario Ministry of the Environment, which publishes a biannual guide to the consumption of a variety of species of fish throughout Ontario based on their age, size, and loading of various contaminants. The data obtained covers mercury levels in perch and walleye from the 1970 up until 1996 (the data varies somewhat by species, location, and frequency of

collection) for the southern end of Lake Huron, Lake St. Clair, and the western and central basins of Lake Erie, presented below in Tables 5-1 through 5-4.

These figures show a number of key points regarding mercury contamination in this region. First of all, it is quickly apparent that the highest levels of mercury are distinctly localised in Lake St. Clair. Secondly, it can be seen that this phenomenon is not linked to processes occurring further upstream in the Great Lakes system which would be reflected in higher mercury levels in fish from Lake Huron, nor are mercury levels appreciably elevated further downstream in Lake Erie, as shown in Figure 5-1.

The data for Lake St. Clair alone over a longer time interval is presented in Figure 5-2, where it can be seen that the levels of mercury in the two major species of yellow perch and walleye have declined drastically since 1970. However the same graph also shows a significant increase in the mercury content of walleye over the period 1988-1995. One possible explanation for this might be that it roughly coincides with the completion of a large municipal incinerator, which went into operation in the Detroit area at about this time. However at this time there is no clear evidence to link these two events and a large number of other factors could be responsible for this change.

5.5 Atmospheric Deposition and Geogenic Sources of Hg to the Environment

Most incidences of elevated mercury concentrations in fish and other wildlife can usually be traced back to a particular point source. In some cases, however, increased mercury concentrations are found in fish and other wildlife in ecosystems, which are remote from industrial point sources (Driscoll et al. 1994). A number of researchers have

Year	Yellow Perch (ug/g)	Walleye (ug/g)
1977	0.22	0.35
1978		
1979		
1980		
1981	0.23	0.47
1982		
1983		0.26
1984		
1985	0.3	0.37
1986		0.32
1987		0.36
1988	0.12	0.27
1989		0.44
1990		0.4
1991	0.19	0.35
1992		0.4
1993		
1994	0.12	0.45

Table 5-1. Mercury Levels in Perch and Walleye in the Southern End of Lake Huron in ug/g. (MOE Data)

Year	Yellow Perch (ug/g)	Walleye (ug/g)
1970	1.94	2.11
1971	1.51	1.78
1972	0.9	1.27
1973	0.45	1.14
1974	0.36	0.98
1975	0.59	0.81
1976	0.98	0.93
1977	0.47	0.99
1978	0.51	0.65
1979	0.49	0.88
1980	0.33	0.91
1981	0.29	0.72
1982	0.29	0.73
1983	0.46	0.57
1984	0.36	0.54
1985	0.22	0.49
1986	0.27	0.48
1987	0.28	0.38
1988	0.26	0.37
1989	0.33	0.54
1990	0.23	0.58
1991	0.23	0.63
1992		0.55
1993	0.24	0.74
1994	0.27	0.87
1995		0.84
1996	0.29	0.62

Table 5-2. Mercury Levels in Perch and Walleye for Lake St. Clair in ug/g. (MOE Data)

Year	Yellow Perch (ug/g)	Walleye (ug/g)
1977		0.3
1978		
1979		0.27
1980		
1981		0.19
1982		0.18
1983		0.24
1984	0.09	0.14
1985		0.12
1986		0.2
1987		0.12
1988		0.14
1989	0.08	0.2
1990		0.14
1991		0.13
1992		0.21
1993	0.06	0.1
1994		0.19
1995		0.17

Table 5-3. Mercury in Perch and Walleye from the Western Basin of Lake Erie in ug/g. (MOE Data)

Year	Yellow Perch (ug/g)	Walleye (ug/g)
1979	0.07	
1980		
1981		
1982		0.14
1983		0.22
1984	0.05	0.21
1985		0.07
1986		0.22
1987		0.09
1988		0.11
1989	0.07	0.12
1990		
1991		0.11
1992	0.07	0.22
1993	0.08	0.16
1994		
1995		0.17
1996	0.04	0.12

Table 5-4. Mercury Levels in Perch and Walleye from the Central Basin of Lake Erie in ug/g. (MOE Data)

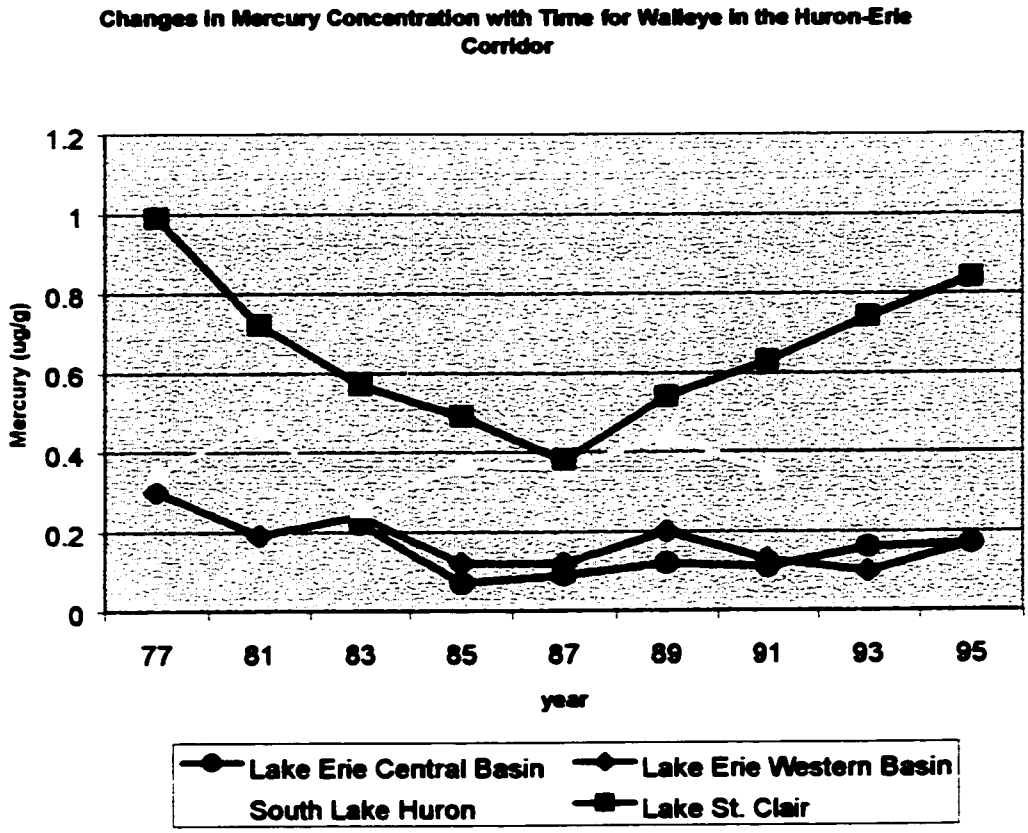

Figure 5-1. Comparative plot showing mercury levels in Walleye for the southern end of Lake Huron, Lake St. Clair, and the western and central basin of Lake Erie in ug/g Hg from 1977-1995. (MOE Data)

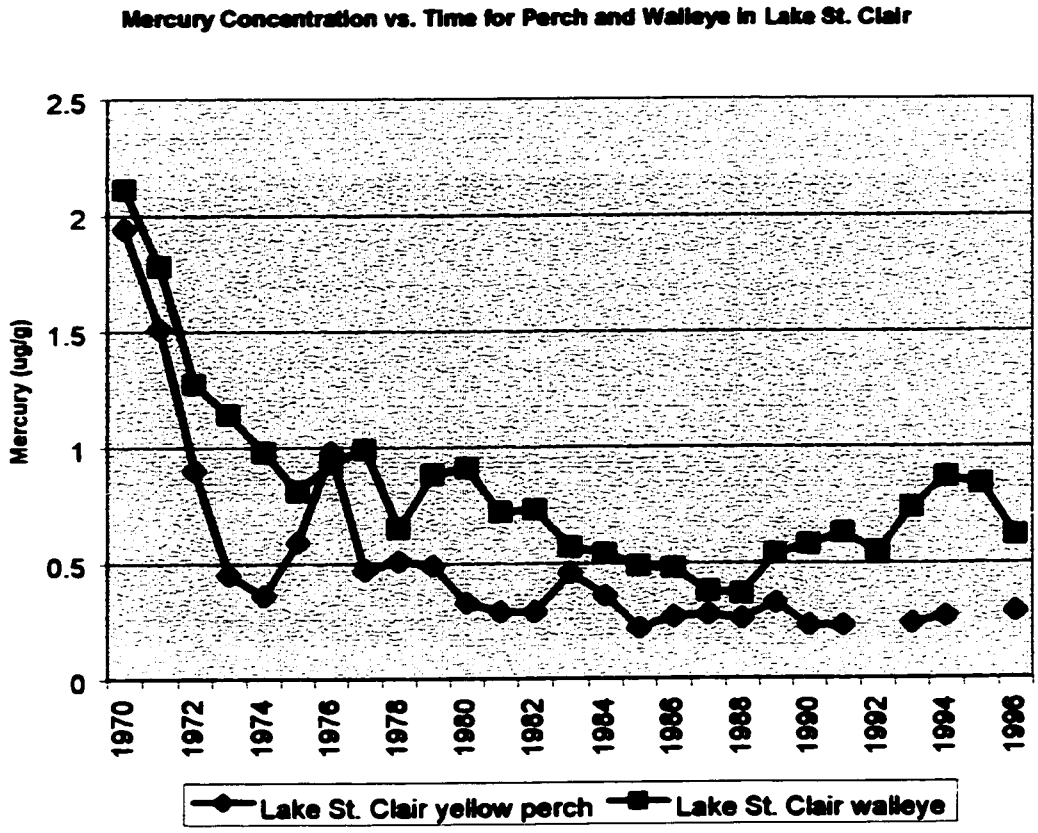

Figure 5-2. Changes in Mercury Concentration with Time for Sport Fish in Lake St. Clair in ug/g Hg from 1970-1996. (MOE Data)

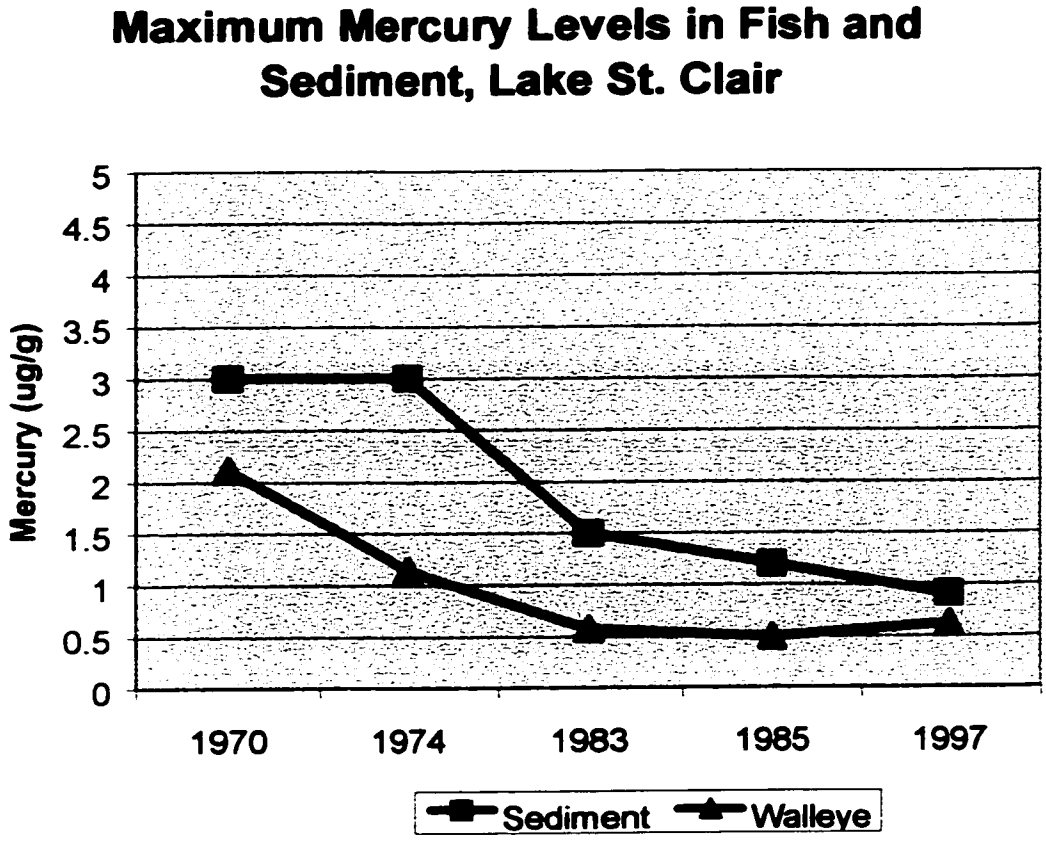

Figure 5-3. Maximum mercury concentrations reported in sediments and walleye in Lake St. Clair in ug/g Hg from 1970-1997

pointed to a relative lack of research aimed at quantifying the contributions of mercury from natural vs. anthropogenic sources (Rasmussen et al. 1998). This can clearly be seen from the disparate numbers reported by federal environmental agencies in Canada and the U.S.A.

In Canada, industrial emissions of mercury to the atmosphere have decreased from about 39 tonnes/year in 1985 to 20 tonnes/year in 1990 (Rasmussen et al. 1998). At the same time, it has been estimated by the Canadian Environmental Protection Service that the annual flux of mercury to the atmosphere from natural sources was on the order of about 3500 tonnes per year for Canada (as quoted in Rasmussen et al. 1998). However, the authors of this report also indicated that this number only included elemental mercury (Hg^0) and not particulate fluxes, and that it was intended to serve only as an order-of-magnitude approximation and to provide a framework within which more accurate data could be added. Meanwhile, the EPA estimates that U.S. emissions of mercury by human activities rival or exceed natural inputs (Hanisch, 1998). Total U.S. anthropogenic emission from all identified sources was estimated to be 158 tons/year for 1994-95. Of this total, approximately 80% was due to the combined output of electric utilities, municipal and medical waste incineration, and commercial and industrial boilers (Hanisch, 1998). Computer models of the atmospheric deposition and dispersion of this mercury indicate that approximately one-third of it, or 47 tons, is deposited within the U.S., and the remaining two-thirds is transported beyond its borders. At the same time, the model estimated that 32 tons of mercury from the global mercury pool was also deposited within the U.S. (Hanisch, 1998)

Clearly, this wide discrepancy in the estimations of the relative amounts of anthropogenic and natural mercury emissions to the ecosystem by neighboring government agencies makes it glaringly obvious how poorly understood the whole phenomenon is. In addition to understanding and quantifying the influence and effects of industrial activity, more geoscience research is needed to improve our understanding of the biogeochemical cycling of mercury species released from common sulphide minerals and other crustal sources (Rasmussen et al. 1998).

It has been shown that in some cases, elevated mercury concentrations in lake sediments in areas that are in reasonable proximity to human activities bear little or no relation to anthropogenic sources at all. A study of mercury distribution in the Muskoka-Haliburton region of Ontario (Rasmussen et al. 1998) showed that there was a wide variation of mercury concentrations in the sediments of lakes that were in close proximity to each other, ranging from <5 ppb to >450 ppb. Within this area, the spatial pattern of mercury concentrations in pre-colonial sediments (>800 years old) mirrored that pattern of concentrations found in modern surficial sediments, indicating that natural processes are governing the distributions of mercury within these lakes. The study found that the surface-to-depth mercury concentration ratio is about the same for all of the lakes despite the variation in mercury concentration among the different lakes. This did not appear to be satisfactorily explained by an atmospheric loading model, and it was concluded that in this area the two-to-five fold surface enrichment phenomenon would be more consistent with diagenetic processes rather than atmospheric deposition.

However, it is generally accepted that situations such as this are the exception rather than the norm, and there is clear evidence for widespread global dispersion of

atmospheric pollutants, as witnessed by the presence of PCBs in the high arctic far removed from any possible sources.

5.6 Airborne Mercury From Local Sources

A study of atmospheric transport and deposition of mercury in the Detroit area suggested that when Lake St. Clair was affected by air masses with an urban origin (i.e. downwind from Detroit), it would receive an average mercury dry deposition flux of 57pg/m^{2}h. A study of the historic trends of airborne trace metals in the Detroit area from 1971-1992 showed that there were nearly 1700 operating incinerators in the vicinity, including two major facilities that were constructed in the 1980s which had a combined capacity in excess of 100 tonnes per hour. One of these, the Detroit Incinerator started operation in 1989, and is one of the largest municipal solid waste incinerators in the U.S. (Pirrone et al. 1996). This study showed that while ambient mercury concentrations decreased at a rate of approximately 7.4% per year from 1971-1981, they then increased again by 10.6% per year from 1982 to 1992, using 1971 and 1982 as the reference year for each of these trends, respectively.

The results from the Detroit study can be compared with results that show the ambient Hg concentrations have increased by 1.5% per year on average for North America during the period 1977-1990. Analysis of lake sediments and dated soils suggests that mercury deposition may have doubled during the last century (Pirrone et al. 1996).

Similarly, in western Canada a study was conducted of atmospheric fallout and natural variations in background mercury gradients in sediments and soils around a smelter in Flin Flon, Manitoba. The results indicated that there was a large circular "bulls-eye" mercury anomaly around the smelter with a radius of approximately 40km, and at a distance of 100km from the stack, emissions from the smelter were indistinguishable from background levels (Rasmussen et al. 1998). This study supported the theory that mercury emissions remain airborne for relatively short distances, in the range of tens of kilometers, which supports the argument that localized deposition of mercury emissions along the Huron-Erie corridor is a significant contributor.

CHAPTER SIX

CONCLUSIONS AND RECOMMENDATIONS

6.1 Mercury in the Lake St. Clair environment

While the levels of mercury contamination in Lake St. Clair have decreased significantly over the last two decades, this system still remains an area of concern, especially since this waterway serves as a recreational area and source of drinking water for so many people. A summation of this and previous studies shows how, in general, mercury levels in both fish and sediments have declined. These same data also show, however, that the rate of decline has decreased significantly, such that the mercury present in the system now may remain there for an extended period of time. Furthermore, recent evidence indicates that mercury in fish may be increasing slightly again over the last eight years after reaching a minimum in the mid-1980's.

This study is the first positive indication of the presence of methylmercury in the sediments of this system, and clearly indicates that conditions for methylating inorganic mercury exist. In turn, this study shows why the presence of mercury (as methylmercury) in fish within the lake continues to be a problem three decades after the major influx of inorganic mercury was halted when the chlor-alkali cells were shut down.

6.2 Continued Input of Atmospheric Mercury

While the source of the original large-scale mercury contamination has been removed, it is important to note that the system is still not entirely free of mercury input.

Atmospheric deposition from industrial and fossil fuel sources inject hundreds of tonnes of mercury into the air over North America every year. Due to the intense industrialization of the Great Lakes basin, a significant proportion of this is emitted in close proximity to the study area. Atmospheric deposition of mercury has been shown to be the source of mercury in ecosystems far-removed from industrial activity, via pathways of long-range atmospheric transport. While these same airborne processes are also at work here, on a smaller scale increased localized deposition of heavier or larger particulate matter that is not as amenable to removal from the region would be expected.

6.3 Continued Bioaccumulation in Fish

Based on these past and present sources of mercury, it is apparent that the Lake St. Clair ecosystem, and fish in particular, will retain some level of mercury contamination. It may even be possible that the rate of atmospheric deposition may be enough to sustain present levels of Hg loading in the system, or at least keep them from attaining any further significant decrease over the long-term. In addition, it is clear that remnant effects of the original mercury spill are still present, as can be seen by the elevated levels of Hg in the sediments of the south-eastern basin of the lake, where the highest amounts of Hg have been historically found since this problem first came to light.

It should also be noted, in reference to the previous data presented on the levels of mercury in various fish species in the Huron – Erie corridor, that no reliable data exist for the period of time before the 1970's, and therefore it is difficult to estimate what the actual "background" level for habitat in this region might be. The fish data compiled here

seems to indicate that the mercury levels are not likely to decline much further, since they now seem to be fluctuating between 0.5-1ppm over a several year period. However, changes on a time scale of this magnitude may be related to other activities or influences, such as variation in the water level or major dredging of the shipping channel.

6.4 Overall Evaluation of Methylmercury Analytical Method Development

Overall, the methods used performed reasonably well, given the difficult nature of methylmercury extraction and analysis. The Grignard derivatization step worked well and was a key "breakthrough" of the method development phase of this project. The method for extraction from the sediment sample needs more work, as evidenced by the low recoveries seen during this project as well as the number of abandoned attempts before applying a technique that had at least marginal success. Other reagents and newer, high-performance methods, particularly those involving elevated temperature and pressures, such as Super-Critical Fluid Extraction and Accelerated Solvent Extraction, are definitely worth investigating in comparison to the techniques already attempted here.

The GC-AED instrumentation performed well, with acceptably low limits of detection and good sensitivity. It also had excellent linearity and good reproducibility. More experimentation with other capillary columns and, particularly, different sample injection options might be beneficial once the extraction from the sediment has been further optimized.

Clearly, there is an imperative need for a robust, widely applicable methylmercury determination method that can be applied to a wide variety of environmental sample types. Mercury cycling in the environment is still very poorly

understood, and the inability to trace organic mercury compounds through the ecosystem leaves an important gap in understanding how these compounds affect the world around them. Some international agencies, particularly the IAEA (International Atomic Energy Agency) in Europe had taken some steps towards this by producing a certified reference material for methylmercury in sediments in the past (which is no longer in production and was unobtainable at the time of the present study), but more needs to be done. Given the amounts of mercury still being released to the environment in North America each year, more emphasis needs to be placed on determining the source, transport, and fate of organomercury compounds on this continent.

6.5 Recommendations for Future Research

As mentioned in the preceding section, there are not at present well-accepted, optimized methods for extraction or analysis of methylmercury in existence. Furthermore, the natural production and subsequent cycling of methylmercury in the environment before its uptake into the higher trophic levels of the food chain is still very poorly understood.

Better quantification of the sediments of Lake St. Clair, such as relating methylmercury to grain size, major element content (C, H, N, S, O) and trace metals might also reveal useful trends and associations in relation to these other variables. Analyses of both of these last two parameters, the major and trace elements, had been planned as a part of this project but were not completed due to time constraints.

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VITA AUCTORIS

NAME:	Andrew David Toms
BIRTH:	Grand Falls, Newfoundland, 1972
EDUCATION:	B.Sc., Memorial University of Newfoundland, St. John's Newfoundland, 1996
	M.Sc., University of Windsor, Windsor, Ontario, 1999